Synthesis and characterization of perhalophenyltin derivatives. Study of their reactivity toward phosphine gold(I) chlorides

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A B S T R A C T

The (perhalophenyl)tin derivatives [SnR$_4$] (**1–3**) and [SnR$_3$Cl] (**4–6**) (R = C$_6$F$_5$, C$_6$F$_3$Cl$_2$, C$_6$Cl$_5$) were prepared from SnCl$_4$ and LiR or [SnR$_4$] in the appropriate molar ratio, while the dinuclear complexes [SnR$_3$]$_2$ (**7–9**) were obtained by treatment of [SnR$_3$Cl] with potassium under toluene reflux. Complexes **2**, **6**·0.5toluene and **7** were structurally characterized, the latter displaying a Sn–Sn bond of 2.808(7) Å, which indicates a strong tin–tin bond with covalent character in solid state. The hexaaryldistannanes **7–9** undergo transmetallation reactions with gold(I) derivatives, such as [AuCl(PPh$_3$)] or [(AuCl)$_2$(μ-dppm)], affording the neutral species [AuR(PPh$_3$)] (**10–12**) or [(AuR)$_2$(μ-dppm)] (**13–15**) or the ionic product [Au$_3$Cl$_2$(μ-dppm)$_2$][Sn(C$_6$F$_5$)$_3$Cl$_2$] (**16**). The crystal structures of **14**·CH$_2$Cl$_2$, **15** and **16**·2CH$_2$Cl$_2$ were determined by X-ray diffraction, the latter showing a Au$_3$ nearly equilateral triangular core in the cation with gold–gold contacts of 3.128(7) and 3.227(12) Å. The main difference between the molecular structures of **14**·CH$_2$Cl$_2$ and **15** (both of them displaying intramolecular gold–gold contacts of 3.142(6) and 3.160(4) Å, respectively) is the presence of an intermolecular Au···Au interaction of 3.2126(8) Å in the case of the C$_6$F$_3$Cl$_2$ complex that gives rise to a tetranuclear unit.

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1. Introduction

Perhalophenyl groups C$_6$X$_5$ (X = F, Cl) have been widely used in the preparation of stable organotransition metal compounds [1], and also provide an enhancement of the Lewis acidity in main group derivatives [2], making the later ones effective catalysts in organic synthesis [2,3]. Among the organotin derivatives, only those with pentafluorophenyl groups were synthesized and studied, *i.e.* the structurally characterized tetrakis(pentafluorophenyl)tin [4] showed no catalytic activity in Mukaiyama-aldol reaction of ketene silyl acetal, while replacement of one or two C$_6$F$_5$ groups by halides (bromine or chlorine) considerably improved its activity [3].

Although [SnR$_3$]$_2$ (R = alkyl, aryl or other organic moiety) are well known compounds [5–9], and give versatile reactions with cleavage of the Sn–Sn single bond by chemical oxidation [10–12], insertion [13], addition [14], and cross-coupling reactions with aryl halides [10,15], hexaorganodistannanes with perhalophenyl groups have not been studied yet. Both the chemical oxidation and the cross-coupling reaction afford the corresponding triorganotin halide, but in the latter process the heteroleptic tetraorganotin derivative, which is further used *i.e.* in fluorous labelling strategy [16], is also obtained.

On the other hand, compounds with gold–tin interactions have been prepared through acid–base reactions between phosphine-gold(I) electrophiles and tin nucleophiles, such as SnCl$_2$ or [SnB$_{11}$H$_{11}$]$^{2-}$ [17–20]. In the last years, our group is focused in the synthesis and study of the properties of complexes with metal–metal interactions, also usually employing an acid–base synthetic strategy. Thus, we were interested in the synthesis of perhalophenyltin compounds, which would presumably present a higher Lewis acidic tin centre than in complexes with different organic substituents, and that, in principle, may behave as strong Lewis acids *versus* d^{10} transition metal compounds, resulting in the formation of species with metallophilic interactions. Thus, we prepared the organotin derivatives [SnR$_4$] (**1–3**), [SnR$_3$Cl] (**4–6**) and [SnR$_3$]$_2$ (**7–9**) (R = C$_6$F$_5$, C$_6$F$_3$Cl$_2$, C$_6$Cl$_5$) and studied their reactivity against [AuCl(PPh$_3$)] or [(AuCl)$_2$(μ-dppm)]. In contrast with what was expected, only some of them react and undergo transmetallation reactions, affording the neutral species [AuR(PPh$_3$)] (**10–12**) or [(AuR)$_2$(μ-dppm)] (**13–15**) or the ionic [Au$_3$Cl$_2$(μ-dppm)$_2$][Sn(C$_6$F$_5$)$_3$Cl$_2$] (**16**).

2. Results and discussion

2.1. Synthesis and characterization

[Sn(C$_6$F$_5$)$_4$] (**1**) was prepared, according to the method described in the literature [4], by reaction of tin tetrachloride with LiC$_6$F$_5$ (1:4)

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in diethyl ether at low temperature. The dichlorotrifluorophenyl and pentachlorophenyl related products (**2**, **3**) were prepared in the similar manner by the reaction between the corresponding LiR and $SnCl_4$ using Schlenk techniques (Eq. (1)). They were obtained as white (**2**) or pale yellow (**3**) solids soluble in toluene and partially soluble in chlorinated solvents and hexane, and their analytical and spectroscopic data agree with the proposed formulation.

$$4LiR + SnCl_4 \xrightarrow{Et_2O/-60\ °C/1\ h} [SnR_4] + 4LiCl$$
$$R = C_6F_5(\mathbf{1}),\ C_6F_3Cl_2(\mathbf{2}),\ C_6Cl_5(\mathbf{3}) \tag{1}$$
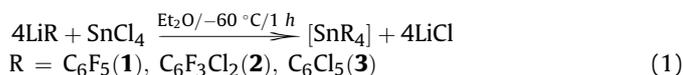
The ^{19}F NMR spectrum of complex **2** shows two singlets located at −95.7 (F_o) and −104.4 ppm (F_p), instead of the singlet at −112.6 ppm that is observed in the ^{19}F NMR spectrum of the free $C_6F_3Cl_3$, indicating that the $C_6F_3Cl_2$ groups are equivalent and bonded to the tin(IV) centre.

None of the mass spectra registered for these compounds shows the molecular ion probably due to the difficulty in ionizing them. A study on the fragmentation and rearrangement processes in the mass spectra of tetrakis(pentafluorophenyl) derivatives of group 4 elements evidenced bond formation with involvement of fluorine abstraction [21]. In the fragmentation of $[Sn(C_6F_5)_4]$ (**1**) the metastable ions $[Sn(C_6F_5)_2F]^+$ and $[Sn(C_6F_5)F_2]^+$ were observed, which is explained by elimination of uncharged C_6F_4 species [21]. In our case the ESI(−) spectrum of **1** shows the peak corresponding to the radical anion $[Sn(C_6F_5)_3]^{-\bullet}$ as the base peak at $m/z = 621$, besides other fragments, such as $[M − 4F]^{-\bullet}$ ($m/z = 712$, 92%), $[Sn(C_6F_5)_2F_3]^-$ ($m/z = 511$, 23%) and $[Sn(C_6F_5)_2F_4]^-$ ($m/z = 530$, 17%). Similarly, the MALDI(−) spectra of **2** and **3** show the ions $[Sn(C_6F_3Cl_2)_3]^{-\bullet}$ ($m/z = 719$) and $[Sn(C_6Cl_5)_2Cl]^-$ ($m/z = 653$), respectively, as the base peak, and the spectrum of **3** also presents a peak assigned to $[Sn(C_6Cl_5)_3]^{-\bullet}$ ($m/z = 866$, 38%).

para and *meta* fluorine atoms, respectively, indicating the equivalence of the aryl groups in the molecule. In the case of complex **5**, the resonances of the fluorine atoms of the $C_6F_3Cl_2$ groups appear at −95.9 (F_o) and −101.7 ppm (F_p) (2:1), which indicates an up-field shift for the singlet of the *para* fluorine atoms if compared with the spectrum of **2**, due to the presence of the chlorine atom in **5**.

We have observed in our compounds that their mass spectra often show species formed by the loss of the halogen atom. Both the MALDI(−) mass spectra of **4** and **5** show the ion $[M − Cl]^{-\bullet}$ at $m/z = 621$ and 719, respectively, as the base peak. Besides, peaks due to the formation of the fragments $[M − Cl]^{-\bullet}$ ($m/z = 866$, 50%) and $[M-C_6Cl_5]^{-\bullet}$ ($m/z = 653$, 15%) were detected in the MALDI(−) mass spectrum of **6**.

Distannanes are formed in a great variety of reactions, and they can sometimes be isolated as by-products [10], but till date no derivatives with perhalophenyl groups had been described. One would expect that this type of complexes could be difficult to prepare because of the ease of cleavage of the tin−tin bond, even more considering that in the related germanium complex $[Ge(C_6F_5)_3]_2$ the Ge−Ge can be broken more easily than in other hexaorgano-digermane derivatives [23]. In contrast, the three hexaorganodistannanes $[SnR_3]_2$ (R = C_6F_5 (**7**), $C_6F_3Cl_2$ (**8**), $(C_6Cl_5)_3$ (**9**)) could be synthesized through a Tamborski type procedure [24], by treatment of the corresponding triorganotin chloride (**4**−**6**) with potassium under toluene reflux for a prolonged period of time (Eq. (2)) and isolated as white solids soluble in toluene and partially soluble in chlorinated solvents and hexane. For this preparation a sequence involving a reduction of triorganotin halide into triorganotin hydride followed by a $Pd(PPh_3)_4$ promoted decomposition into hydrogen and hexaorgano distannane can be an alternative procedure [25].

$$2[SnR_3Cl] + 2K \xrightarrow[72\ h]{Toluene\ reflux} [SnR_3]_2 + 2KCl$$
$$R = C_6F_5(\mathbf{4}),\ C_6F_3Cl_2(\mathbf{5}),\ C_6Cl_5(\mathbf{6}) \qquad\qquad R = C_6F_5(\mathbf{7}),\ C_6F_3Cl_2(\mathbf{8}),\ C_6Cl_5(\mathbf{9}) \tag{2}$$

Attempts to prepare triorganotin chlorides by reaction of the same starting products in the appropriate molar ratio only led to the expected complex in the case of the pentachlorophenyl derivative $[Sn(C_6Cl_5)_3Cl]$ (**6**), while in the other cases the tetraorganotin compounds **1** and **2** were the only products isolated from the reaction medium (see Scheme 1). Thus, the triorganotin chlorides $[SnR_3Cl]$ (R = C_6F_5 (**4**), $C_6F_3Cl_2$ (**5**), C_6Cl_5 (**6**)) were synthesized by a Kocheskov redistribution reaction [22] between the homoleptic tin complexes $SnCl_4$ and $[SnR_4]$ in a 1:3 molar ratio, process that takes place with a redistribution of ligands (Scheme 1). Complexes **4**−**6** are isolated as white (**4** and **5**) or pale yellow (**6**) air and moisture-stable solids, soluble in toluene and partially soluble in chlorinated solvents and hexane.

The ^{19}F NMR spectrum of the pentafluorophenyl derivative **4** is very similar to that registered for **1**, displaying three resonances at −121.9, −145.0, and −157.2 ppm (2:1:2) for the *ortho*,

The ^{19}F NMR spectra of complexes **7** and **8** display the same pattern than those of the starting products, showing three resonances at −125.6 (F_o), −150.3 (F_p) and −161.8 ppm (F_m) for the pentafluorophenyl complex or two singlets at −94.6 and −104.5 ppm for the trichlorodifluorophenyl one, in both cases significantly shifted if compared to those of the starting products. Although from their ^{19}F NMR spectra it cannot be unambiguously concluded whether the tin−tin bond remains present in solution, the existence of an equilibrium between $[SnR_3]_2$ and $2SnR_3^\bullet$, described for other hexaorganodistannanes [26], can be excluded due to presence of only one set of signals in each case in the absence of other reagents susceptible for transmetallation reactions in solution.

Regarding the mass spectra, the MALDI(−) spectrum of **7** shows the ion $[Sn(C_6F_5)_3]^{-\bullet}$ at $m/z = 621$ as the base peak. In the MALDI(+) spectra of the pentachlorophenyl compound **9** the only fragment detected was $[Sn(C_6Cl_5)_3]^+$, located at $m/z = 866$.

As commented above, we were interested in the study of the reactivity of the tin compounds synthesized with phosphinegold(I) complexes in order to prepare new species with Au···Sn metallophilic interactions or to use the tin compounds as arylating agents. Unfortunately, no reaction was observed between the mononuclear complexes $[SnR_4]$ (**1**−**3**) or $[SnR_3Cl]$ (**4**−**6**) and $[AuCl(PPh_3)]$ or $[(AuCl)_2(\mu$-dppm$)]$, neither to afford complexes with intermetallic contacts nor to observe transmetallation reactions, and the unaltered starting materials were recovered from the reaction medium in all cases.

When the reaction of $[AuCl(PPh_3)]$ with the distannanes **7**−**9** is tested, partial decomposition to metallic gold is observed regardless
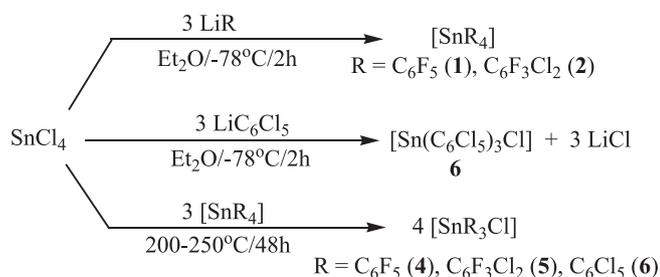
Scheme 1. Synthesis of complexes **1**–**6**.

of the molar ratio employed. In addition, when the Au/Sn molar ratio is 2:1, the transmetallation products [AuR(Ph₃P)] (R = C₆F₅ (**10**), C₆F₃Cl₂ (**11**), C₆Cl₅ (**12**)) can be isolated from the mother liquors after extraction with toluene (**11**, **12**) and hexane (**10**), confirming the ability of the distannanes [SnR₃]₂ to act as arylating agents at gold (see Eq. (3)). Thus, complexes **10**–**12** were obtained as white (**10**, **11**) or pale yellow (**12**) solids, soluble in most common organic solvents and non-soluble in hexane. Complex **10** had already been prepared by a different synthetic method [27].

$$1/2[SnR_3]_2 + 2[AuCl(PPh_3)] \longrightarrow \begin{array}{l} [AuR(PPh_3)] + SnR_2Cl_2 + Au + PPh_3 \\ R = C_6F_5(\mathbf{10}),\ C_6F_3Cl_2(\mathbf{11}),\ C_6Cl_5(\mathbf{12}) \end{array} \qquad (3)$$
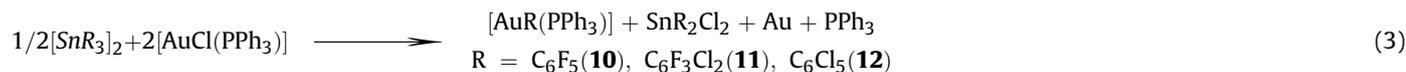
In the ³¹P{¹H} NMR spectra of **11** and **12** the singlet due to PPh₃ appears shifted up-field if compared to the staring material [AuCl(PPh₃)]: from 33.1 to 42.1 (**11**) or 39.5 ppm (**12**), while the ¹⁹F NMR spectrum of **11** displays the typical signals of a dichlorotrifluorophenyl group bonded to gold(I). Both the ESI(+) mass spectra of compounds **11** and **12** show the highly stable cation [Au(PPh₃)₂]⁺ as the base peak at m/z = 721, as well as peaks due to [Au(PPh₃)]⁺ at m/z = 459. The cation [M + Au(PPh₃)]⁺ was also identified in both cases at m/z = 1117 (**11**) and 1167.5 (**12**).

The reactions of the distannanes **7**–**9** with the dinuclear gold(I) species [(AuCl)₂(μ-dppm)] were also carried out in order to evaluate their capability to act as arylating agents and the possibility of obtaining a complex with a Au···Sn interaction. When the reaction of the pentafluorophenyl compound **7** with the gold(I) diphosphine complex is carried out in a 1:1 molar ratio a mixture of products, from which the transmetallation product [{Au(C₆F₅)}₂(μ-dppm)], already known and structurally characterized [28,29], as well as the ionic complex [Au₃Cl₂(μ-dppm)₂][Sn(C₆F₅)₃Cl₂], could be identified at different reaction times. In contrast, if the same reaction takes place in a 1:2 molar ratio, although metallic gold is always observed, independently on the aryl group bonded to tin the transmetallation reaction product [(AuR)₂(μ-dppm)] (R = C₆F₅ (**13**), C₆F₃Cl₂ (**14**), C₆Cl₅ (**15**)) can be isolated as a pure product (Scheme 2). Complexes **14** and **15** are obtained as white (**14**) or pale yellow (**15**) air and moisture-stable solids soluble in most common organic solvents and non-soluble in hexane.

Moreover, the ionic compound [Au₃Cl₂(μ-dppm)₂][Sn(C₆F₅)₃Cl₂] (**16**) could also be isolated as a pure species from the reaction of [Sn(C₆F₅)₃]₂ with [(AuCl)₂(μ-dppm)] in a 1:4 molar ratio and with a shorter reaction period (shorter than 15 min). This complex was obtained as a pale yellow stable solid, which is soluble in chlorinated solvents and acetone, and non-soluble in diethyl ether and hexane. If the other perhalophenyl groups are present in the starting tin compound, the related ionic complexes could not be prepared even with shorter reaction periods, fact that led us to consider the ionic product as a possible intermediate in the reaction pathway.
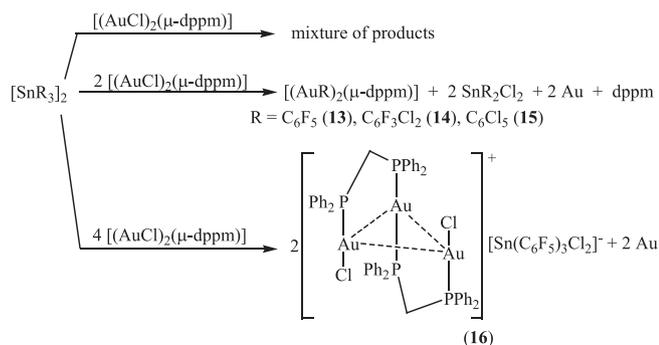
The ³¹P{¹H} NMR spectra of complexes **14** and **15** display a singlet at 32.4 and 31.1 ppm, respectively, while their ¹H NMR spectra show a triplet located at 3.65 and 3.58 ppm, respectively, confirming the presence of the diphosphine. The coordination of the C₆F₃Cl₂ group to gold in **14** is confirmed in its ¹⁹F NMR spectrum by the appearance of two singlets at −90.7 and −116.5 ppm, signals which appear displaced if compared to those of the starting complex **8**, and show similar chemical shifts than in **11**. The base peak in the MALDI(+) mass spectra of **14** and **15**, located at m/z = 977 (**14**) and 1027 (**15**), corresponds to the cation [M − R]⁺, and a peak due to the dinuclear fragment [Au₂dppm₂]⁺ is also observed in both cases at m/z = 1161.

The ionic nature of complex **16** was confirmed by its molar conductivity in acetone, and the presence of dppm in its ³¹P{¹H} and ¹H NMR spectra, which display resonances at 32.4 and 3.64, respectively, similar chemical shifts than in the neutral dinuclear complex **13** (32.1 and 3.67 ppm, respectively). In this case, the resonances of the fluorine atoms in its ¹⁹F NMR spectrum appear at −122.2, −146.1 and −157.5 ppm, indicating that the C₆F₅ ligands are bonded to the tin centre, and also differ from those found in **13** (−116.4, −159.1 [³J$_{F-F}$ = 19.9 Hz] and −163.1 ppm). These signals start to appear with longer reaction periods, suggesting the transfer of C₆F₅ moieties from tin to gold. In the MALDI(+) mass spectrum of **16** gold-containing fragments are observed, and the molecular cation appears as the base peak at m/z = 1429, and also the fragment [Au₂dppm₂]⁺ (m/z = 1161) could be identified. Finally, in its MALDI(−) mass spectrum tin-containing fragments can be detected and, thus, the molecular anion [Sn(C₆F₅)₃Cl₂]⁻ appears at m/z = 691.

Finally, it is of interest to note that this type of reaction is not observed with the corresponding SnR₄ and SnR₃Cl. This different reactivity could be explained by the homoleptic cleavage of the tin–tin bond in the [SnR₃]₂ compounds (**7**–**9**) resulting in the formation of radicals of the type SnR'₃, which have been detected in other cases even in solution [26]. This type of radicals cannot be formed so easily in the case of SnR₄ and SnR₃Cl, what makes them less reactive in these type of reaction. The formation of these radicals could be proved by the careful analysis of their MS spectra. Thus, although both in the cases of the SnR₄ or SnR₃Cl, and [SnR₃]₂ the corresponding MS(−) spectra show the presence of peaks due to the radical anion SnR₃⁻·, in the formers their abundance is very low, while in the case of the hexaorganodistannanes **7** and **9** they appear as the base peak. This seems to indicate that the reactive species is the radical SnR'₃, which in the cases of SnR₄ and SnR₃Cl need stronger conditions to be formed. According with these results, although no reaction mechanism studies were carried out, a radical-chain mechanism [30] could be considered for the transmetallation of the phosphinegold(I) chlorides with the hexaorganodistannanes (**7**–**9**).

2.2. Crystal structures

Single crystals of **2** and **6**·0.5C₇H₈ were obtained by slow evaporation of a toluene solution of the complex at room temperature. The former crystallizes in the space group *I4₁/a* of the tetragonal system, while the latter makes it in the space group *P-1* of the triclinic system and crystallizes with half a molecule of solvent per molecule of compound. Both structures contain the tin centre in a tetrahedral coordination geometry (Figs. 1 and 2), slightly distorted in the case of **6**·0.5C₇H₈, in which the C(1)–Sn–C(11) angle has a value of 118.8(2)°. The Sn–C bond lengths are in

Scheme 2. Synthesis of complexes **13**–**16**.
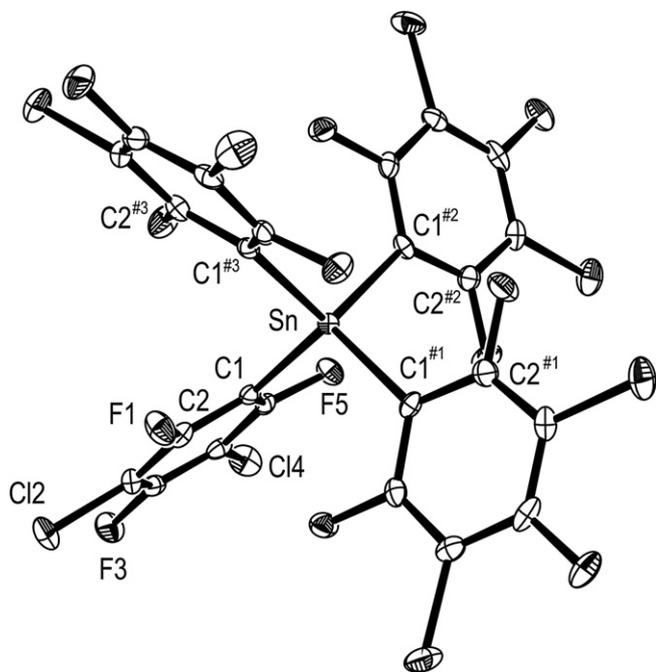
Fig. 1. Molecular structure of **2** with the labelling scheme of the atom positions. Selected bond lengths and angles: Sn–C 2.133(3) Å, C(1)–Sn–C(1)#1 107.48(16), C(1)–Sn–C(1)#2 110.48(8), C(1)–Sn–C(1)#3 110.48(8)°. #1: $-x$, $-y+1/2$, z; #2: $y-1/4$, $-x+1/4$, $-z+1/4$; #3: $-y+1/4$, $x+1/4$, $-z+1/4$.

general longer in **6**·0.5C$_7$H$_8$ (average: 2.163(6) Å) than in **2** (2.133(3) Å), the latter being similar to those found in [Sn(C$_6$F$_5$)$_4$] [4], [SnPh$_4$] [31] or [Sn(*p*-Tol)$_4$] [32] (2.126(8), 2.140(1) or 2.147 Å, respectively), while the former are longer than the Sn–C bond distances in [SnPh$_3$Cl] (2.123 Å) [33] or [Sn(*p*-Tol)$_3$Cl] (av. 2.118 Å) [34] and similar to those described for [SnMes$_3$Cl] (av. 2.158(5) Å)
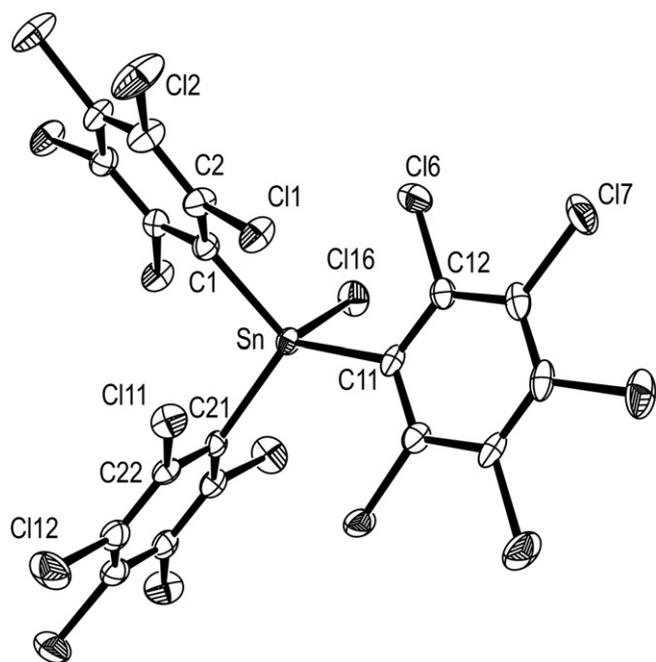
[35]. The comparison of all these Sn–C lengths seems to indicate: first, a higher electron-withdrawing effect for the C$_6$Cl$_5$ group if compared to Cl, which implies that the substitution of a penta-chlorophenyl group for a chlorine decreases the Lewis acidity of the tin centre with a subsequent elongation of the Sn–C distances in spite of the lower steric demand of the chlorine atom; and, second, that both C$_6$Cl$_5$ and Cl are better electron-withdrawers than other aryl groups, such as Tol or Ph. Finally, the Sn–Cl bond length in **6**·0.5C$_7$H$_8$, of 2.335(17) Å, compares well with those found in the related trichloroaryltin chlorides [SnPh$_3$Cl] [33], [Sn(*p*-Tol)$_3$Cl] [34] or [SnMes$_3$Cl] [35] (2.321, 2.373 or 2.386(2) Å, respectively).

Single crystals of [Sn(C$_6$F$_5$)$_3$]$_2$ (**7**) suitable for X-ray diffraction studies were obtained by slow evaporation of a CHCl$_3$ solution of the compound at room temperature. The molecular structure of **7** (Fig. 3) contains two Sn(C$_6$F$_5$)$_3$ units connected through a tin–tin single bond, resulting in a tetrahedral coordination geometry for both tin centers. The Sn–Sn bond length of 2.808(7) Å is close to double the covalent radium of tin (1.40 Å) and significantly shorter the double of its van der Waals radium (2.17 Å) [36], which indicates a strong bond with covalent character in solid state. This is also evident if this distance is compared to those found in other related tin derivatives containing the units C$_3$Sn–SnC$_3$, in which the Sn–Sn bond distances range from 2.72 to 3.08 Å (statistical evaluation made on 32 compounds with Sn–Sn single bond, structures found in the Cambridge Structural Data Base). The C$_6$F$_5$ moieties bonded to the tin atoms are orientated in a gauche conformation, with a torsion angle of 61.4(2)°, and the Sn–C bond lengths in **7** (from 2.142(5) to 2.147(5) Å) are of the same order than in [Sn(C$_6$F$_5$)$_4$] (2.126(8) Å) [4].

Single crystals of compounds **14**·CH$_2$Cl$_2$ and **15** were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane. Both molecular structures display the same disposition than the related derivatives [{Au(C$_6$F$_5$)}$_2$(μ-dppm)] (**13**) [27,28], [{Au(C$_6$F$_5$)}$_2$(μ-P^{i}Pr$_2$CH$_2$PPh$_2$)] [29] and [(AuPh)$_2$(μ-dppm)] [37], all of them showing each gold(I) centre linearly coordinated to an aryl group and to one of the phosphorus atom of the bridging bidentate ligand, as well as intramolecular gold–gold contacts (Figs. 4 and 5). The Au–P bond lengths, 2.270(3) and 2.300(3) Å for **14**·CH$_2$Cl$_2$ and 2.2882(16) and 2.2715(17) Å for **15**, are

Fig. 2. Molecular structure of **6**·0.5C$_7$H$_8$ with the labelling scheme of the atom positions. Selected bond lengths and angles: Sn–C(1) 2.149(6), Sn–C(11) 2.169(6), Sn–C(21) 2.170(6), Sn–Cl(16) 2.3353(17) Å, C(1)–Sn–C(11) 118.8(2), C(1)–Sn–C(21) 105.6(2), C(11)–Sn–C(21) 115.8(2), C(1)–Sn–Cl(16) 104.75(18), C(11)–Sn–Cl(16) 98.40(18), C(21)–Sn–Cl(16) 112.89(17)°.
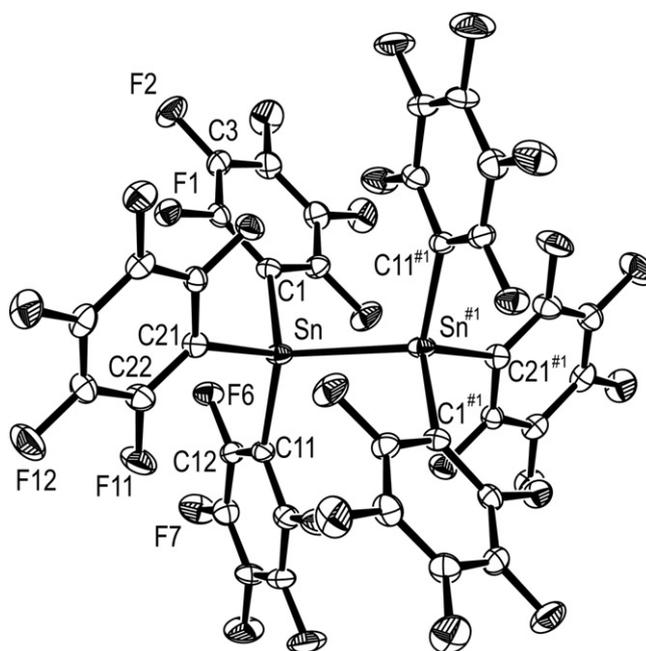
Fig. 3. Molecular structure of **7** with the labelling scheme of the atom positions.

similar to the average Au–P bond distances found in the compounds mentioned above (2.283, 2.273(2) and 2.300 Å in (**13**) [27,28], [{Au(C$_6$F$_5$)}$_2$(μ-P^{i}Pr$_2$CH$_2$PPh$_2$)] [29] and [(AuPh)$_2$(μ-dppm)] [37], respectively). Regarding the Au–C bond lengths, of 2.059(12) and 2.067(12) Å for **14**·CH$_2$Cl$_2$ and 2.057(6) and 2.070(6) Å for **15**, these are also of the same order than those observed in the related species cited above, which range from 2.044(5) to 2.063(6) Å [27,28,37]. The intramolecular gold–gold contacts in **14**·CH$_2$Cl$_2$ and **15**, 3.142(6) and 3.160(4) Å, respectively], compare well with those described in the crystal structures of [{Au(C$_6$F$_5$)}$_2$(μ-dppm)] (**13**) (3.163(11) Å) [27,28] or [(AuPh)$_2$(μ-dppm)] (3.154(1) Å) [37], but are longer than the Au–Au distance in [{Au(C$_6$F$_5$)}$_2$(μ-P^{i}Pr$_2$CH$_2$PPh$_2$)] [29] (3.093(3) Å), which contains a different bridging ligand [33]. The peculiarity of **14**·CH$_2$Cl$_2$ is the evidence of an additional longer gold–gold contact of 3.2126(8) Å between the gold atoms of two neighbouring molecules, supported by two additional hydrogen bonds [H(23)–F5#1 = 2.415(7), C(23)–F5#1 = 3.342(7) Å, C(23)–H(23)–F5#1 = 173.7(7)] none of them present in the crystal structure of **15**.

Finally, single crystals of complex **16**·2CH$_2$Cl$_2$ suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a dichloromethane solution of the compound. It crystallizes in *Ibca* space group of the orthorhombic system with two molecules of CH$_2$Cl$_2$ for molecule of complex and only half a molecule and one CH$_2$Cl$_2$ in the asymmetric unit. The crystal structure of **16**·2CH$_2$Cl$_2$ confirms its ionic nature showing isolated cations [Au$_3$Cl$_2$(μ-dppm)$_2$]$^+$ (Fig. 6) and anions [Sn(C$_6$F$_5$)$_3$Cl$_2$]$^-$ (Fig. 7). The structure of the cation had already been established and reported in previous works with different anions: [Au(C$_6$F$_5$)$_3$Cl]$^-$ [38], Cl$^-$ [39], ClO$_4^-$ [40], PF$_6^-$ [41], and it exhibits a triangular Au$_3$ core with intermolecular aurophilic interactions between the three metals of 3.1282 (7) (two of them) and 3.2268(12) Å. The same trend in the Au–Au distances is observed in other salts, which display distances of 3.1525(4), 3.1922(4) and 3.2770(4) Å in the hexafluorophosphate [41], 3.0663(5), 3.1645(5) and 3.6784(4) Å in the [Au(C$_6$F$_5$)$_3$Cl]$^-$ derivative [38], 3.076(1) (two distances) and 3.729(1) Å in the chloride [39] and 3.0883(8), 3.1738(6) and 3.4500(8) Å in the

Fig. 5. Molecular structure of **15** with the labelling scheme of the atom positions. Hydrogen atoms have been omitted for clarity.

Fig. 4. Molecular structure of **14**·CH$_2$Cl$_2$ with the labelling scheme of the atom positions. Hydrogen atoms have been omitted for clarity.
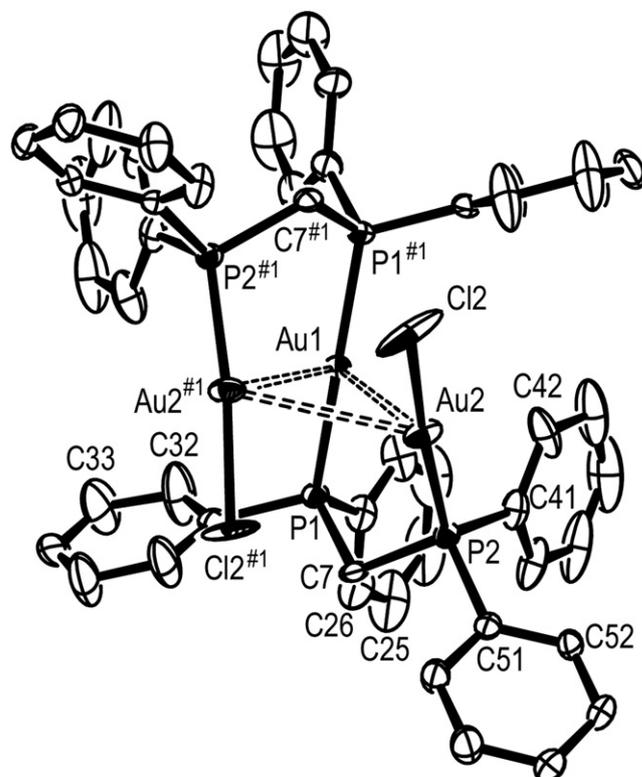
Fig. 6. Crystal structure of the cation of **16**·2CH$_2$Cl$_2$ with the labelling scheme of the atom positions. Hydrogen atoms have been omitted for clarity.
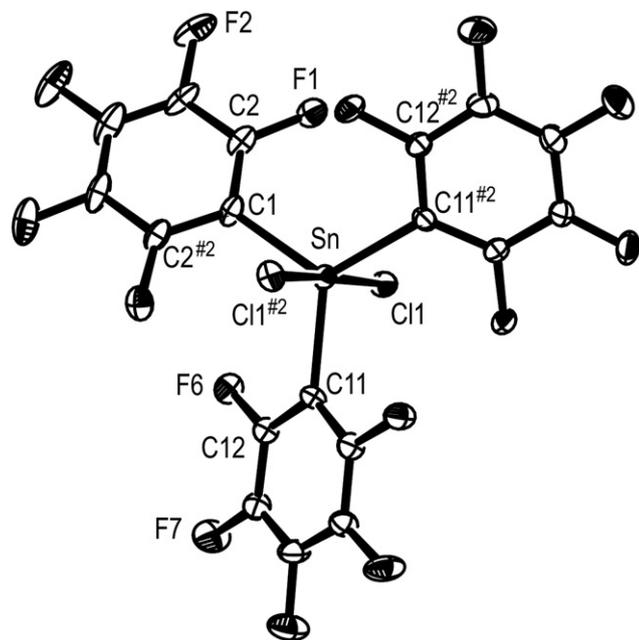
Fig. 7. Crystal structure of the anion of **16**·2CH$_2$Cl$_2$ with the labelling scheme of the atom positions.

perchlorate [40]. As can be deduced from these distances, only in **16**·2CH$_2$Cl$_2$ and in the hexafluorophosphate salt the three gold atoms maintain aurophilic contacts, while in the rest only two Au⋯Au interactions are observed. The Au–Cl and Au–P bond lengths in the cation of **16**·2CH$_2$Cl$_2$ are 2.315(3) Å, and 2.218(3) and 2.318(3) Å, respectively, the latter indicating a higher *trans* influence for the phosphorus donor ligand than for the chloride, as had also been observed in the other salts [38–41].

The structure of the anion in **16**·2CH$_2$Cl$_2$ contains the tin centre in a trigonal bipyramidal environment with the chlorine atoms occupying the apical positions and the aryl groups in the equatorial plane. The Sn–C$_{ipso}$ bond lengths (2.140(16) and 2.157(11) Å) compare well with those found in [Sn(C$_6$F$_5$)$_4$] (2.126(8) Å) [4], in **2** (2.133(3) Å) and in the hexaoragonodistannane **7** (2.142(5)–2.147(5) Å). In contrast, the Sn–Cl bond length in **16**·2CH$_2$Cl$_2$ (2.498(3) Å) is longer than in the pentachlorophenyl derivative **6**·0.5C$_7$H$_8$ (2.3353(17) Å).

The importance of hydrogen bonding in crystal packing has been discussed [42] and in the case of [Au$_3$Cl$_2$(μ-dppm)$_2$][PF$_6$], where hydrogen bonding involving the anions in is extensive, it has been concluded that the hydrogen-bonded interactions in the lattice have a certain influence on the geometry of the Au$_3$ cluster in salts containing the cation [Au$_3$Cl$_2$(μ-dppm)$_2$]$^+$ [41]. A closer look into the crystal packing of **16**·2CH$_2$Cl$_2$ also evidenced an extensive hydrogen bonding network, in which the cation, the anion and the solvent molecule are involved.

3. Conclusions

The perhalophenyltin derivatives (**1–6**) showed no reactivity toward the phosphine gold(I) chlorides, indicating that, although the perhalophenyl groups increase the Lewis acidity of the tin centre, they do not increase their Lewis acidity as much as necessary to react with gold(I) precursors.

The hexaorganodistannanes (**7–9**) behave in a different manner than expected, and their reactivity toward phosphine gold(I) chlorides showed their ability to transfer the perhalophenyl moiety, making them potential candidates as arylating agents for gold(I). Only in the case of the pentafluorophenyl derivative **7** a different

result is obtained when the Au/Sn ratio is modified in its reaction with [(AuCl)$_2$(μ-dppm)], leading to a ionic complex with a gold cation and a tin anion.

This different behaviour could be explained by the easier homoleptic cleavage of the tin–tin bond in [SnR$_3$]$_2$, resulting in the formation of radicals of the type SnR$_3^•$ observed in their MS spectra, than in the case of SnR$_4$ and SnR$_3$Cl, making the latter less reactive and suggesting a radical-chain mechanism for the transmetallation reactions.

4. Experimental

4.1. Instrumentation

All manipulations with the organotin compounds were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were collected from an MBraun MB SPS-800 distillation column before use. The ^{19}F, 1H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker ARX 300 spectrometer in CDCl$_3$. The MS-ESI spectra were recorded with a microOTOF-Q-Bruker, using the ESI technique. The MALDI mass spectra were registered on a Microflex Bruker spectrometer using DIT (Dithranol) as matrix. The m/z values are given for the higher peak in the isotopic pattern, and the used equipment did not allow an unambiguous discrimination between ions and radical ions. The C, H analyses were carried out with a Perkin-Elmer 240C microanalyzer.

4.2. General

Sn(C$_6$F$_5$)$_4$ (**1**) [4], [AuCl(PPh$_3$)] [43] and [(AuCl)$_2$(μ-dppm)] [44] were synthesized according to literature procedures. No reaction was observed between the mononuclear complexes [SnR$_4$] (**1–3**) or [SnR$_3$Cl] (**4–6**) and [AuCl(PPh$_3$)] or [(AuCl)$_2$(μ-dppm)], under the general reaction conditions: CH$_2$Cl$_2$ as solvent, room temperature and 1 h mixing.

4.3. Synthesis of [SnR$_4$] (R = C$_6$F$_3$Cl$_2$ (**2**), C$_6$Cl$_5$ (**3**))

Complexes **2** and **3** were prepared following a similar procedure to that reported for **1** [4]. A freshly prepared solution of LiR [13 mmol; 2.68 g (**2**), 3.33 g (**3**)] in diethyl ether at −60 °C was added dropwise to a cooled (−60 °C) diethyl ether suspension of SnCl$_4$ (3.26 mmol, 0.85 g). The reaction mixture was stirred at that temperature for 1 h and then allowed to slowly warm to room temperature and stirred for 8 h. The resulted white suspension was evaporated to dryness in vacuum and 30 mL of toluene added. After removal of the LiCl by filtration, the solution was concentrated to 5 mL and the products crystallized as white (**2**) or pale yellow (**3**) solids.

4.3.1. Compound (2)
Yield: 80%. Elemental analysis (%) calcd for C$_{24}$Cl$_8$F$_{12}$Sn: C 31.38; found: C 31.44. ^{19}F NMR (300 MHz, CDCl$_3$, ppm): δ −95.7 (s, 8F, F$_o$) and −104.4 (s, 4F, F$_p$). MS-MALDI(−) m/z (%): 719 [Sn(C$_6$F$_3$Cl$_2$)$_3$]$^{-•}$ (100).

4.3.2. Compound (3)
Yield: 86%. Elemental analysis (%) calcd for C$_{24}$Cl$_{20}$Sn: C 25.83; found: 26.01. MS-MALDI(−) m/z (%): 653 [Sn(C$_6$Cl$_5$)$_2$Cl]$^-$ (100), 866 [Sn(C$_6$Cl$_5$)$_3$]$^{-•}$ (38).

4.4. Synthesis of [SnR$_3$Cl] (R = C$_6$F$_5$ (**4**), C$_6$F$_3$Cl$_2$ (**5**), C$_6$Cl$_5$ (**6**))

Method A: 0.2 mmol of SnCl$_4$ (0.023 mL) and 0.6 mmol of [SnR$_4$] (R = C$_6$F$_5$, 0.47 g; R = C$_6$F$_3$Cl$_2$, 0.56 g; R = C$_6$Cl$_5$, 0.67 g) were mixed in a schlenck under argon atmosphere and the mixture was stirred at reflux temperature for 48 h. Toluene was then added to the

reaction mixture and evaporation of the solvent led to the product as a white (**4** and **5**) or pale yellow (**6**) crystalline solid.

Method B: Complex **6** can alternative be prepared as follows: a freshly prepared diethyl ether solution of $Li(C_6Cl_5)$ (13 mmol, 3.35 g) at $-78\ °C$ was added dropwise to a cooled suspension of $SnCl_4$ (4.3 mmol, 1.13 g) in the same solvent. The reaction mixture was stirred at that temperature for 2 h and then allowed to slowly warm to room temperature while stirring for 12 more hours. The resulting yellow solution was evaporated to dryness in vacuum, and the remaining solid extracted with toluene (30 mL). After removal of the LiCl formed by filtration, the toluene solution was concentrated to 5 mL, which leads to the crystallization of **6** as a pale yellow solid.

4.4.1. Compound (*4*)

Yield: 84%. Elemental analysis (%) cacld for $C_{18}ClF_{15}Sn$: C 32.99; found C 32.56. ^{19}F NMR (300 MHz, $CDCl_3$, ppm): $\delta -121.9$ (m, 6F, F_o), -145.0 (t, 3F, F_p, $^3J_{Fp-Fm} = 19.9$ Hz), -157.2 (m, 6F, F_m). MS-MALDI $(-)$ m/z (%): 621 $[M - Cl]^{-\bullet}$ (100).

4.4.2. Compound (*5*)

Yield: 51%. Elemental analysis (%) cacld for $C_{18}Cl_7F_9Sn$: C 28.67; found C 28.59. ^{19}F NMR (300 MHz, $CDCl_3$, ppm): $\delta -95.9$ (s, 6F, F_o), -101.7 (s, 3F, F_p); MS-ESI$(-)$ m/z (%): 719 $[M - Cl]^{-\bullet}$ (100).

4.4.3. Compound (*6*)

Yield: 64%. Elemental analysis (%) cacld for $C_{18}Cl_{16}Sn$: C 23.96; found C 23.87. MS-ESI$(-)$ m/z (%): 653 $[M - C_6Cl_5]^{-\bullet}$ (15), 866 $[M - Cl]^{-\bullet}$ (50).

4.5. Synthesis of $[SnR_3]_2$ (R = C_6F_5 (*7*), $C_6F_3Cl_2$ (*8*), C_6Cl_5 (*9*))

To a toluene solution of 1 mmol of $[SnR_3Cl]$ (0.66 g (**4**), 0.76 g (**5**) or 0.91 g (**6**)) an excess of potassium (1.28 mmol, 0.05 g) was added and the reaction mixture was stirred under reflux for 72 h. The followed KCl formed and the excess of potassium were then filtered off and the resulting pale yellow solution was concentrated by evaporation in vacuum, and the hexaorganodistannanes were isolated as white crystalline solids.

4.5.1. Compound (*7*)

Yield: 46%. Elemental analysis (%) cacld for $C_{36}F_{30}Sn_2$: C 34.88; found: C 33.99. ^{19}F NMR (300 MHz, $CDCl_3$, ppm): $\delta -125.6$ (m, 12F, F_o), -150.3 (t, 6F, F_p, $^3J_{Fp-Fm} = 19.8$ Hz), -161.8 (m, 12F, F_m). MS-MALDI$(-)$ m/z (%): 621 $[Sn(C_6F_5)_3]^{-\bullet}$ (100).

Table 1
Details of data collection and structure refinement for complexes **2**, **6**·0.5C$_7$H$_8$ and **7**.

Compound	**2**	**6**·0.5C$_7$H$_8$	**7**
Formula	$C_{24}Cl_8F_{12}Sn$	$C_{21.5}Cl_{20}Sn$	$C_{36}F_{30}Sn_2$
Formula weight	918.53	948.14	1239.74
Crystal system	Tetragonal	Triclinic	Triclinic
Space group	$I4_1/a$	$P-1$	$P-1$
a (Å)	18.2659(16)	8.6675(5)	9.6823(3)
b (Å)	18.2659(16)	11.2763(6)	10.6163(4)
c (Å)	8.5992(7)	18.1720(9)	10.8894(4)
$\alpha(°)$	90	92.763(3)	99.896(2)
$\beta(\&deg)$	90	103.050(3)	113.346(2)
$\gamma(°)$	90	94.451(3)	108.891(2)
V (Å^3)	2869.1(4)	1721.04(16)	2256(5)
Z	4	2	1
T (K)	120(2)	120(2)	120(2)
μ(Mo Kα)(mm^{-1})	1.733	2.000	1.554
Reflections collected	7349	12338	13237
R(int)	0.0756	0.0426	0.0479
Unique reflections	1739	6574	4302
GOF on F^2	1.017	1.059	1.123
Final R indices[$I > 2\sigma(I)$]: R1, wR2	0.0398, 0.0662	0.0509, 0.1435	0.0489, 0.1173

Table 2
Details of data collection and structure refinement for complexes **14**·CH$_2$Cl$_2$, **15** and **16**·2CH$_2$Cl$_2$.

Compound	**14**·CH$_2$Cl$_2$	**15**	**16**·2CH$_2$Cl$_2$
Formula	$C_{38}H_{22}Au_2Cl_6F_6P_2$	$C_{37}H_{22}Au_2Cl_{10}P_2$	$C_{70}H_{48}Au_3Cl_8F_{15}P_4Sn$
Formula weight	1261.1	1276.92	2291.15
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	C2/c	P-1	Ibac
a (Å)	12.1549(4)	10.0208(7)	21.3816(8)
b (Å)	23.3186(7)	13.6820(14)	23.8841(9)
c (Å)	28.3386(9)	16.0957(15)	32.4186(10)
$\alpha(°)$	90	98.419(5)	90
$\beta(\&deg)$	101.6060(10)	101.343(5)	90
$\gamma(°)$	90	110.234(5)	90
V (Å^3)	7867.9(4)	1974.2(3)	16555.5(10)
Z	8	2	8
T (K)	120(2)	120(2)	120(2)
μ(Mo Kα)(mm^{-1})	7.997	2.148	6.006
Reflections collected	29501	19343	60210
R(int)	0.0880	0.0640	0.0971
Unique reflections	9343	8889	9903
GOF on F^2	1.087	1.023	1.044
Final R indices[$I > 2\sigma$ (I)]: R1, wR2	0.0693, 0.1887	0.0430, 0.0993	0.0704, 0.2271

4.5.2. Compound (*8*)

Yield: 43%. Elemental analysis (%) cacld for $C_{36}Cl_{12}F_{18}Sn_2$: C 30.09; found: C 29.96. ^{19}F NMR (300 MHz, $CDCl_3$, ppm): $\delta -94.6$ (s, 12F, F_o), -104.5 (s, 6F, F_p).

4.5.3. Compound (*9*)

Yield: 65%. Elemental analysis (%) cacld for $C_{36}Cl_{30}Sn_2$: C 24.95; found: C 24.35. MS-MALDI$(-)$ m/z (%): 866 $[Sn(C_6Cl_5)_3]^{-\bullet}$ (100).

4.6. Synthesis of $[AuR(PPh_3)]$ (R = C_6F_5 (*10*) $C_6F_3Cl_2$ (*11*), C_6Cl_5 (*12*))

To a dichloromethane solution of $[AuCl(PPh_3)]$ (0.5 mmol, 0.25 g) 0.125 mmol of the corresponding $[SnR_3]_2$ (0.157 g (**7**), 0.181 g (**8**) or 0.219 g (**9**)) was added at room temperature. After 30 min of stirring the solvent was evaporated in vacuum, 20 mL of toluene were then added, and the metallic gold formed was filtered off. The remaining solution was concentrated and hexane (20 mL) was added to precipitate the new complex as a white (**10** and **11**) or pale yellow (**12**) solid.

4.6.1. Compound (*10*)

Yield: 63%.

4.6.2. Compound (*11*)

Yield: 51%. Elemental analysis (%) cacld for $C_{24}H_{15}AuCl_2F_3P$: C 43.71, H 2.29; found: C 43.62, H 2.19. $^{31}P\{^1H\}$ NMR (300 MHz, $CDCl_3$, ppm): $\delta 42.1$ (s). ^{19}F NMR (300 MHz, $CDCl_3$, ppm): $\delta -90.2$ (s, 2F, F_o), -116.3 (s, 1F, F_p). ^1H NMR (300 MHz, $CDCl_3$, ppm): $\delta 7.40-7.66$ (m,

Table 3
Selected bond lengths [Å] and angles [°] for complex **7**.

Sn–C(1)	2.147(5)
Sn–C(11)	2.142(5)
Sn–C(21)	2.144(5)
Sn–Sn#1	2.8081(7)
C(11)–Sn–C(21)	109.24(16)
C(11)–Sn–C(1)	107.70(17)
C(21)–Sn–C(1)	110.26(17)
C(11)–Sn–Sn#1	111.88(12)
C(21)–Sn–Sn#1	109.38(12)
C(1)–Sn–Sn#1	108.36(12)

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

Table 4
Selected bond lengths [Å] and angles [°] for complex **14**·CH$_2$Cl$_2$.

Au(1)−C(1)	2.059(12)
Au(2)−C(11)	2.067(12)
Au(1)−P(1)	2.300(3)
Au(2)−P(2)	2.270(3)
Au(1)−Au(2)	3.1422(6)
Au(1)−Au(1)#1	3.2126(8)
C(1)−Au(1)−P(1)	171.3(3)
C(1)-Au(1)-Au(2)	92.3(3)
P(1)−Au(1)−Au(2)	88.68(7)
C(1)−Au(1)−Au(1)#1	82.9(2)
P(1)−Au(1)−Au(1)#1	100.68(7)
Au(2)−Au(1)−Au(1)#1	149.01(2)
C(11)−Au(2)−P(2)	175.3(3)
C(11)−Au(2)−Au(1)	94.9(3)
P(2)−Au(2)−Au(1)	89.79(7)

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

15H, C$_6$H$_5$). MS-ESI(+) *m/z* (%): 459 [Au(PPh$_3$)]$^+$ (25), 721 [Au(PPh$_3$)$_2$]$^+$ (100), 1117 [M+Au(PPh$_3$)]$^+$ (6).

4.6.3. Compound (12)

Yield: 60%. Elemental analysis (%) cacld for C$_{24}$H$_{15}$AuCl$_5$P: C 40.66, H 2.13; found: C 40.56, H 2.05. ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$, ppm): δ 39.5 (s). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 7.38−7.71 (m, 15H, C$_6$H$_5$). MS-ESI(+) *m/z* (%): 459 [Au(PPh$_3$)]$^+$ (23), 721 [Au(PPh$_3$)$_2$]$^+$ (100), 1167 [M + Au(PPh$_3$)]$^+$ (2).

4.7. Synthesis of [(AuR)$_2$(μ-dppm)] (R = C$_6$F$_5$ (13), C$_6$F$_3$Cl$_2$ (14), C$_6$Cl$_5$ (15))

To a dichloromethane solution of [(AuCl)$_2$(μ-dppm)] (0.2 mmol, 0.16 g) the corresponding hexaorgano distannane (0.1 mmol, 0.124 g (**7**); 0.141 g (**8**); 0.17 g (**9**)) was added at room temperature. After stirring for 30 min and filtering off the metallic gold formed, the solution was evaporated to ca 5 mL, and the product was precipitated with hexane as a white (**13** and **14**) or pale yellow (**15**) solid.

4.7.1. Compound (13)
Yield: 62%.

4.7.2. Compound (14)

Yield: 75%. Elemental analysis (%) cacld for C$_{37}$H$_{20}$Au$_2$Cl$_4$F$_6$P$_2$: C 37.76, H 1.71, found C: 37.70, H 1.69. ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$, ppm): δ 32.4 (s). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 3.65 (t, 2H, CH$_2$, $^2J_{PH}$ = 11 Hz), 7.39−7.67 (m, 20H, C$_6$H$_5$). ^{19}F NMR (300 MHz, CDCl$_3$, ppm): δ −90.7 (s, 4F, F$_o$), −116.5 (s, 2F, F$_p$). MS-MALDI(+) *m/z* (%): 977 [M − C$_6$F$_3$Cl$_2$]$^+$ (100), 1161 [Au$_2$dppm$_2$]$^+$ (9).

Table 5
Selected bond lengths [Å] and angles [°] for complex **15**.

Au(1)−C(1)	2.070(6)
Au(1)−P(1)	2.2882(16)
Au(1)−Au(2)	3.1602(4)
Au(2)−C(11)	2.057(6)
Au(2)−P(2)	2.2715(17)
C(1)−Au(1)−P(1)	175.55(17)
C(1)−Au(1)−Au(2)	101.78(16)
P(1)−Au(1)−Au(2)	79.27(5)
C(11)−Au(2)−P(2)	174.67(17)
C(11)−Au(2)−Au(1)	89.35(16)
P(2)−Au(2)−Au(1)	94.18(5)

Table 6
Selected bond lengths [Å] and angles [°] for complex **16**·2CH$_2$Cl$_2$.

Au(1)−Au(2)	3.1282(7)
Au(2)−Au(2)#1	3.2268(12)
Au(1)−P(1)	2.318(3)
Au(2)−P(2)	2.218(3)
Au(2)−Cl(2)	2.315(3)
Sn−C(1)	2.140(16)
Sn−C(11)	2.157(11)
Sn−Cl(1)	2.498(3)
P(1)#1−Au(1)−P(1)	172.79(16)
P(2)−Au(2)−Cl(2)	171.83(12)
Au(2)#1−Au(1)−Au(2)	62.10(2)
Au(1)−Au(2)−Au(2)#1	58.952(12)
Cl(1)#2−Sn−Cl(1)	175.20(15)
C(1)−Sn−C(11)	118.1(3)
C(11)−Sn−C(11)#2	123.8(6)
C(11)−Sn−Cl(1)#2	89.2(3)
C(1)−Sn−Cl(1)	92.40(7)
C(11)−Sn−Cl(1)	88.6(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y, -z + 1/2$ #2 $-x + 3/2, y + 0, -z + 1$.

4.7.3. Compound (15)

Yield: 67%. Elemental analysis (%) cacld for C$_{37}$H$_{22}$Au$_2$Cl$_{10}$P$_2$: C 34.78, H 1.74; found: C 34.69, H 1.66. ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$, ppm): δ 31.1 (s). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 3.58 (t, 2H, CH$_2$, $^2J_{PH}$ = 11 Hz), 7.39−7.72 (m, 20H, C$_6$H$_5$). MS-MALDI(+) *m/z* (%): 1027 [M − C$_6$Cl$_5$]$^+$ (100), 1161 [Au$_2$dppm$_2$]$^+$ (38).

4.8. Synthesis of [Au$_3$Cl$_2$(μ-dppm)$_2$][Sn(C$_6$F$_5$)$_3$Cl$_2$] (16)

To a solution of [(AuCl)$_2$(μ-dppm)] (0.2 mmol, 0.16 g) in CH$_2$Cl$_2$ at room temperature **4** (0.05 mmol, 0.061 g) was added. The reaction mixture was stirred for 15 min, the metallic gold formed was filtered off, and the resulting pale yellow solution was evaporated, obtaining complex **16** as a pale yellow solid. Yield: 49%. Elemental analysis (%) cacld for C$_{70}$H$_{48}$Au$_3$Cl$_8$F$_{15}$P$_4$Sn: C 36.67, H 2.11; found: C 36.60, H 2.04. ^{31}P{^{1}H} NMR (300 MHz, CDCl$_3$, ppm): δ 32.4 (s). ^{19}F NMR (300 MHz, CDCl$_3$, ppm): δ −122.2 (m, 6F, F$_o$), −146.1 (m, 3F, F$_p$, $^3J_{Fp−Fm}$ = 19.8 Hz), −157.5 (m, 6F, F$_m$); ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 3.64 (m, 4H, CH$_2$), 7.39−7.67 (m, 40H, C$_6$H$_5$). MS-MALDI(+) *m/z* (%): 1161 [Au$_2$dppm$_2$]$^+$ (70), 1429 [Au$_3$Cl$_2$(μ-dppm)$_2$]$^+$ (100). MS-MALDI(−) *m/z* (%): 691 [Sn(C$_6$F$_5$)$_3$Cl$_2$]$^−$ (85). Λ$_M$ (acetone) = 102 Ω$^{−1}$ cm^2 mol$^{−1}$.

4.9. Crystallography

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Nonius Kappa CCD diffractometer equipped with an Oxford Instruments low temperature attachment. Data were collected using monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Scan type ω and φ. Absorption corrections: semiempirical (based on multiple scans). The structures were refined on F^2 using the program SHELXL-97 [45]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included using a riding model. Further details of the data collection and refinement are given in Tables 1 and 2 and main bind distances and angles in Tables 3−6.

Acknowledgement

Appendix A. Supplementary material

CCDC 779061-779066 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc.cam.ac.uk/data_request/cif.

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