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# Photoinitiated Reactions of Haloperfluorocarbons with Gold(I) Organometallic Complexes. Perfluoroalkyl Gold(I) and Gold(III) Complexes

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**Abstract:** The study of perfluoroalkyl metal complexes is key to understanding and improving metal-promoted perfluoroalkylation reactions. Herein we report the synthesis of the first gold complexes with primary or secondary perfluoroalkyl ligands by photoinitiated reactions between Au(I) organometallic complexes and iodoperfluoroalkanes. Complexes of the types  $LAuR_F$  ( $L = PPh_3$  or  $N,N$ -bis(2,6-diisopropylphenyl)imidazol-2-ylidene;  $R_F = n-C_4F_9$ ,  $n-C_6F_{13}$ ,  $i-C_3F_7$ ,  $c-C_6F_{11}$ ) and  $[Au(R_F)(Ar)](PPh_3)$  ( $Ar = 2,4,6$ -trimethylphenyl) have been isolated and characterized. Alkynes  $R_F-C\equiv CR$  were formed by reaction of  $Ph_3PAu-C\equiv CR$  ( $R = Ph$ ,  $nHex$ ) with  $IR_F$  ( $R_F = n-C_4F_9$ ,  $i-C_3F_7$ ). Evidences of a photoinitiated radical mechanism for these reactions have been obtained. Au(III) complexes  $[Au(n-C_4F_9)(X)(Y)L]$  ( $X = Y = Cl, Br, I, Me$ ;  $X = Me, Y = I$ ) have been prepared or in situ generated, and their thermal or photochemical decomposition reactions have been studied.

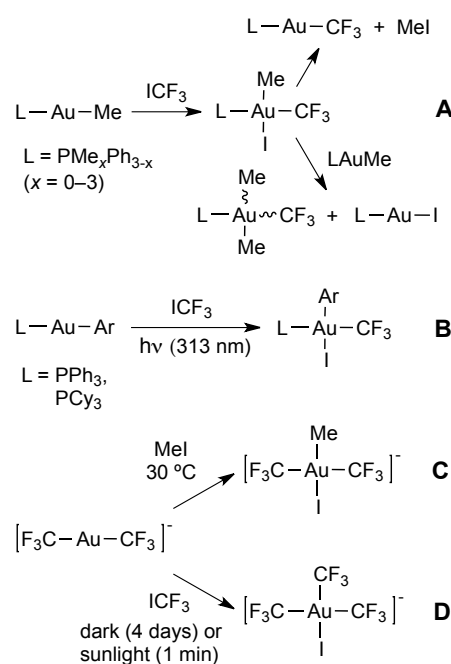
## Introduction

The industrial demand for fluorinated organic compounds<sup>[1]</sup> has boosted intensive research on metal-mediated or -catalysed perfluoroalkylation reactions during the last two decades.<sup>[2]</sup> In many of these reactions, reductive elimination is often proposed as the final step, in which perfluoroalkylated organic products are released from the metal coordination sphere.<sup>[2b, 3]</sup> However, it is generally accepted that perfluoroalkyl complexes present a pronounced inertness against reductive elimination<sup>[4]</sup> and, consequently, a very limited number of stoichiometric C–perfluoroalkyl bond-forming reductive eliminations have been observed. Reported examples comprise aryl-trifluoromethyl-Pd(II) complexes containing purposely designed ligands,<sup>[3c, 3j, 5]</sup> or alkyl- and aryl-trifluoromethyl complexes of metals in high oxidation states, such as Pd(IV),<sup>[6]</sup> Ni(IV),<sup>[7]</sup> Cu(III)<sup>[3b, 8]</sup> or Au(III).<sup>[9]</sup>

In contrast to the thoroughly studied trifluoromethyl complexes, metal complexes containing larger perfluoroalkyl ligands have received much less attention.<sup>[3i, 10]</sup> Interest for this type of compounds arise from their applications in the

perfluoroalkylation of organic substrates,<sup>[3i, 11]</sup> in the synthesis of highly fluorinated small molecules and fluoropolymers,<sup>[12]</sup> or in C–F bond activation.<sup>[13]</sup> Likewise, whereas a relatively large number of trifluoromethyl Au complexes have been reported,<sup>[9b, 9d, e, 14]</sup> no complexes containing heavier perfluoroalkyl groups bonded to Au have been isolated or fully characterized. To fill this gap and to increase the knowledge on the chemistry of metal perfluoroalkyls, we started a project aimed at synthesizing and studying the reactivity of Au(I) and Au(III) complexes containing perfluoroalkyl ligands different than trifluoromethyl.

Perfluoroalkyl iodides ( $IR_F$ ) were chosen as perfluoroalkyl sources because of their commercial availability and reactivity against metal complexes in low oxidation states.<sup>[10b, 15]</sup> Pioneering studies by Puddephatt and co-workers showed that complexes  $LAuMe$  react with  $ICF_3$  to give Au(III) and/or Au(I) trifluoromethyl complexes depending on L (Scheme 1, **A**).<sup>[16]</sup> To explain the observed reaction products, they proposed that the initially formed  $[Au(CF_3)(Me)(L)]$  undergoes reductive elimination of MeI or ligand exchange reactions to give the final products. Evidences for a radical mechanism were obtained, but the photochemical character of the reaction was not investigated.



**Scheme 1.** Reported oxidative addition reactions of  $ICF_3$  to Au(I) complexes.

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Glockling obtained  $\text{Ph}_3\text{PAuCF}_3$  in the reaction between  $\text{Ph}_3\text{PAu}(\text{CH}(\text{SiMe}_3)_2)$  and  $\text{ICF}_3$ .<sup>[17]</sup> Toste and co-workers studied the reactions of complexes of the type  $\text{R}_3\text{PAuAr}$  ( $\text{R} = \text{Ph}, \text{Cy}$ ) and  $\text{ICF}_3$  under UV irradiation (Scheme 1, **B**). These reactions gave Au(III) complexes of the type  $[\text{Au}(\text{CF}_3)(\text{Ar})(\text{PR}_3)]$  by a radical chain mechanism. Mechanistic studies suggested that the reaction is initiated by one electron transfer from the starting Au(I) complex to a photoexcited  $\text{ICF}_3$  molecule.<sup>[9c]</sup> The isolated Au(III) trifluoromethyl complexes were photostable, but they thermally decompose to give ArI and  $\text{R}_3\text{PAuCF}_3$ . Interestingly, the reaction of  $[\text{Au}(\text{CF}_3)(\text{Ar})(\text{PR}_3)]$  with  $\text{Ag}^+$  gave cationic complexes which underwent fast reductive elimination of  $\text{ArCF}_3$ .<sup>[9c]</sup> Shen and co-workers observed a similar fast reductive elimination of  $4\text{-FC}_6\text{H}_4(\text{CF}_2\text{H})$  in the reaction of  $[\text{Au}(\text{CF}_2\text{H})(4\text{-FC}_6\text{H}_4)\text{Cl}(\text{PCy}_3)]$  with  $\text{Ag}^+$ .<sup>[9a]</sup> Recently, the oxidative additions of MeI or  $\text{ICF}_3$  to  $(\text{PPh}_4)[\text{Au}(\text{CF}_3)_2]$  to give  $(\text{PPh}_4)[\text{Au}(\text{CF}_3)_2(\text{CX}_3)]$  were reported by the groups of Toste ( $\text{X} = \text{H}$ )<sup>[9b]</sup> and Menjón ( $\text{X} = \text{F}$ )<sup>[14e]</sup> (Scheme 1, **C** and **D**). The latter group also observed by  $^{19}\text{F}$  NMR the formation of *trans*- $[\text{Au}(\text{CF}_3)_2(n\text{-C}_4\text{F}_9)]$  in the analogous reaction with  $n\text{-C}_4\text{F}_9\text{I}$ .

In this work we report a study of the reactivity of Au(I) organometallic complexes of the type  $\text{LAuR}$  ( $\text{L} = \text{PPh}_3, N,N\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazol-2-ylidene}$  (IPr);  $\text{R} = \text{methyl}, \text{aryl}$  or *alkynyl*) with perfluoroalkyl iodides. These reactions take place under photoactivation with a mild light source and afford Au(I) or Au(III) perfluoroalkyl complexes, or R-R<sub>F</sub> coupling products. These reactions have allowed the isolation and structural characterization of the first Au(I) and Au(III) complexes with primary and secondary perfluoroalkyl ligands. Preliminary results on the stability and reactivity of Au(III) complexes containing a perfluoroalkyl and an aryl or alkyl ligand are presented.

## Results and Discussion

### Reactions of Au(I) alkyl complexes with iodoperfluorocarbons

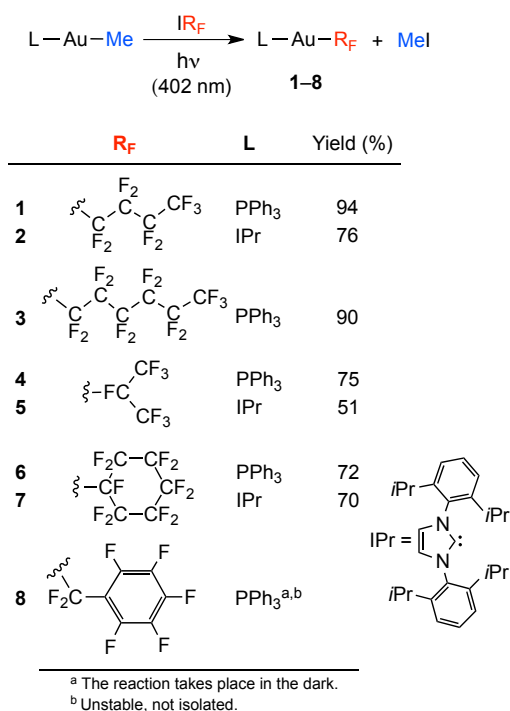
When a solution of  $\text{Ph}_3\text{PAuMe}$  and perfluoro-1-iodobutane in  $\text{CD}_2\text{Cl}_2$  was irradiated with a 402 nm LED for 1 min, a quantitative reaction to give MeI and  $\text{Ph}_3\text{PAu}(n\text{-C}_4\text{F}_9)$  (**1**) took place (Scheme 2). The same products were formed after irradiation with a UV fluorescent lamp ( $\lambda_{\text{max}} = 310$  nm), but in this case traces of ethane were observed, likely arising from photolysis of  $\text{Ph}_3\text{PAuMe}$ .<sup>[18]</sup> On heating at 60 °C in the dark ( $\text{CDCl}_3$ ) the reaction was slower (the yield was 59% after 20 min) and partial decomposition to give metallic gold also took place. No reaction was observed in the dark after 30 min at room temperature, or when the reaction mixture was irradiated with a blue LED ( $\lambda_{\text{max}} = 454$  nm).

Analogously,  $\text{IPrAuMe}$  and  $n\text{-C}_4\text{F}_9\text{I}$  did not react in the dark, but quantitatively gave MeI and  $\text{IPrAu}(n\text{-C}_4\text{F}_9)$  (**2**) upon irradiation at 402 nm (Scheme 2). The tertiary alkyl complex  $\text{IPrAu}t\text{Bu}$  reacted similarly with  $n\text{-C}_4\text{F}_9\text{I}$ , to give *t*BuI and **2**. The reactions of  $\text{LAuMe}$  ( $\text{L} = \text{Ph}_3\text{P}, \text{IPr}$ ) with the secondary iodoperfluoroalkane  $i\text{-C}_3\text{F}_7\text{I}$  proceeded in the same way, to give  $\text{LAu}(i\text{-C}_3\text{F}_7)$  ( $\text{L} = \text{PPh}_3$  (**4**), IPr (**5**)). Remarkably, no reaction

intermediates were observed by NMR spectroscopy in any of these reactions.

Au(I) perfluoroalkyl complexes **1–7** (Scheme 2) were isolated in 51–94% yield after irradiating a solution of the corresponding  $\text{LAuMe}$  and  $\text{IR}_F$  in  $\text{CH}_2\text{Cl}_2$  with the 402 nm LED. The only significant by-product detected was  $\text{IPrAuI}$ , which was formed in the reaction of  $\text{IPrAuMe}$  with  $c\text{-C}_6\text{F}_{11}\text{I}$  in a 10% yield and was separated from **7** by column chromatography. The isolated Au(I) perfluoroalkyl complexes are air and light stable white solids, except  $\text{Ph}_3\text{PAu}(n\text{-C}_6\text{F}_{13})$  (**3**), which was obtained as an air-sensitive colourless oil. To the best of our knowledge, complexes **6** and **7** are the first metal complexes reported containing the perfluorocyclohexyl ligand.

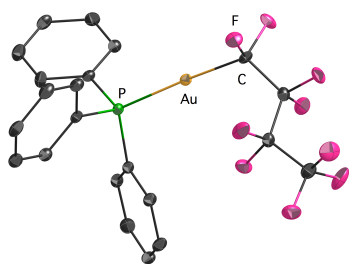
$\text{Ph}_3\text{PAuMe}$  reacted with  $\text{C}_6\text{F}_5\text{CF}_2\text{I}$  in the dark to give **8** (Scheme 2), which partially decomposed upon isolation to give an impure oil and metallic gold particles. The reaction of  $\text{IPrAuMe}$  with  $\text{C}_6\text{F}_5\text{CF}_2\text{I}$  gave a mixture containing  $\text{IPrAuI}$ , likely  $\text{IPrAu}(\text{CF}_2\text{C}_6\text{F}_5)$ , and several unidentified products, which were not separated.



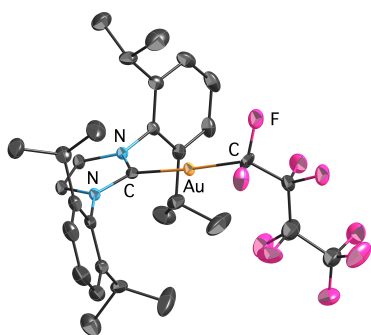
**Scheme 2.** Reactions of Au(I) methyl complexes with iodoperfluorocarbons.

The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction (Figures 1 and 2). In both complexes the gold atoms show a slightly distorted linear coordination environment. The  $\text{Au}(n\text{-C}_4\text{F}_9)$  unit presents an "L" conformation in both cases, probably to allow a more efficient molecular packing. The Au–CF<sub>2</sub> bond is slightly shorter in **1** (2.097(2) Å) than in **2** (2.125(3) Å), and both Au–CF<sub>2</sub> distances are longer than the Au–CF<sub>3</sub> distances reported for similar Au(I)

trifluoromethyl complexes containing NHC or phosphine ligands (2.01–2.08 Å).<sup>[19]</sup>



**Figure 1.** Crystal structure of **1** in the solid state (50% thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Au-C 2.097(2), Au-P 2.2918(5); C-Au-P 173.07(6).

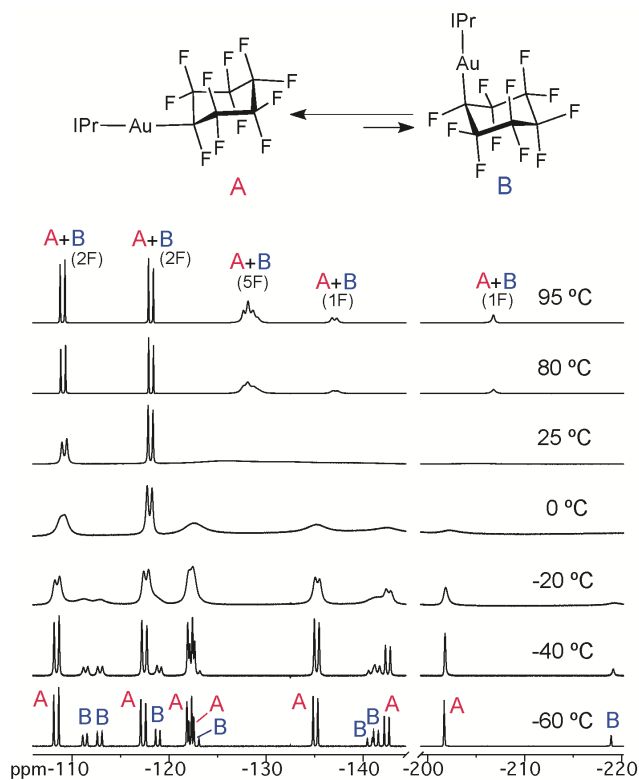


**Figure 2.** Molecular structure of **2** in the solid state (50% thermal ellipsoids). Selected bond lengths and angles: Au-C<sub>carbene</sub> 2.014(2), Au-CF 2.125(3); C<sub>carbene</sub>-Au-CF 175.89(10).

The <sup>19</sup>F and <sup>31</sup>P NMR spectra of **1**, **3**, **4** and **8** show the expected <sup>31</sup>P-<sup>19</sup>F coupling patterns, with <sup>3</sup>J<sub>PF</sub> values in the range of 12.1–26.4 Hz. In complex **6** the <sup>31</sup>P-<sup>19</sup>F coupling was not resolved because of exchange broadening (see below).

Perfluorocyclohexyl complexes **6** and **7** exist as mixtures of two conformers, which could be observed by NMR spectroscopy at low temperature. Fast exchange between both conformers gave rise to coalescence of their <sup>19</sup>F or <sup>31</sup>P NMR signals into a single set of averaged signals. The <sup>19</sup>F NMR spectrum of **7** at -60 °C showed two sets of signals (Figure 3). According to the symmetry of the conformers, each of these sets was composed by six doublets, corresponding to the unequivalent equatorial and axial CF<sub>2</sub> fluorine nuclei, and a singlet, corresponding to the AuCF. The large splittings of these doublets (249–317 Hz) arise mainly from the geminal F-C-F coupling.<sup>[20]</sup> The AuCF signals appear around -200 and -219 ppm as singlets. One of the two sets of signals is more intense than the other, and therefore was assigned to the less sterically hindered conformer, having the LAu moiety in equatorial disposition. According to this assignment, the AuCF appear at a higher δ value in the main conformer (LAu<sub>eq</sub>-C-F<sub>ax</sub>) than in the minor one (LAu<sub>ax</sub>-C-F<sub>eq</sub>). This is in agreement with previous <sup>19</sup>F NMR studies on

substituted perfluorocyclohexanes, which show that the axial fluorine nuclei are less shielded than the equatorial ones.<sup>[21]</sup> Complex **6** shows a similar behaviour and its spectra are included in the Supporting Information (Figure S1).



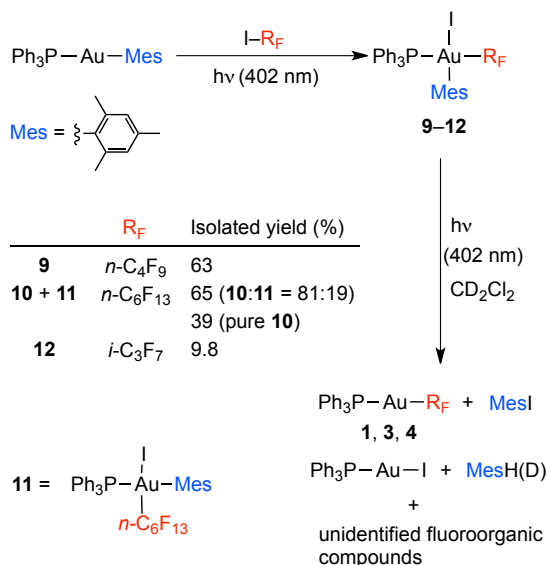
**Figure 3.** Variable-temperature <sup>19</sup>F NMR spectra of **7** (D<sub>8</sub>-Toluene, 564.6 MHz).

### Reactions of Au(I) aryl complexes with iodoperfluorocarbons

Ph<sub>3</sub>PAuMes (Mes = 2,4,6-trimethylphenyl) did not react with *n*-C<sub>4</sub>F<sub>9</sub>I in the dark at room temperature (CD<sub>2</sub>Cl<sub>2</sub>) or at 60 °C (CDCl<sub>3</sub>). However, upon irradiation at 402 nm the starting materials gradually transformed into the oxidative addition product [Au(*n*-C<sub>4</sub>F<sub>9</sub>)(Mes)I(PPh<sub>3</sub>)] (**9**, Scheme 3). At short irradiation times (ca. 1–2 min), **9** was the main reaction product, along with unreacted starting materials and smaller amounts of **1**, MesI, Ph<sub>3</sub>PAuI, mesitylene and several unidentified organofluorine products. Prolonged irradiation led to a progressive decay of **9** in favour of the other reaction products, which became finally the main components of the mixture (Figures S5–S7). Complex **9** was isolated in 63% yield after irradiating a mixture of Ph<sub>3</sub>PAuMes and *n*-C<sub>4</sub>F<sub>9</sub>I for 90 seconds. Its crystal structure was determined by X-ray diffraction (Figure 4).

In CD<sub>2</sub>Cl<sub>2</sub> solution, **9** is stable at room temperature in the dark, but decomposed upon irradiation at 402 nm to give a mixture containing essentially the same products which were previously observed after prolonged irradiation of the reaction

mixture (Figure S8). This suggests that these reaction products arose from photodecomposition of **9**. Remarkably, integration of the  $^1\text{H}$  NMR spectrum and GC-MS analysis of the obtained mixture revealed that the mesitylene formed after photodecomposition of **9** in  $\text{CD}_2\text{Cl}_2$  was partially deuterated in one of the aromatic positions.

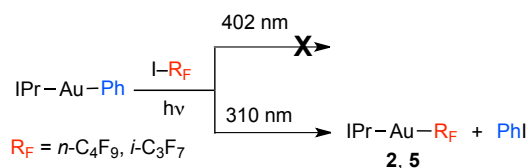


**Scheme 3.** Reactions of  $\text{Ph}_3\text{PAuMesAu(I)}$  with iodoperfluoroalkanes and photodecomposition of the resulting Au(III) complexes.

The outcome of the reaction of  $\text{Ph}_3\text{PAuMes}$  with  $n\text{-C}_6\text{F}_{13}\text{I}$  was similar. However, in this case a mixture of two isomeric Au(III) complexes (**10** and **11**) was isolated (Scheme 3). The main isomer (**10**) was obtained pure by recrystallization in a 39% yield. Its X-ray structure showed the same configuration as for **9** (Figure 5). Owing to its higher solubility, the minor isomer (**11**) could not be isolated free of **10**, and its NMR data suggest that the  $\text{PPh}_3$  and Mes ligands are mutually placed in *trans* (see below).

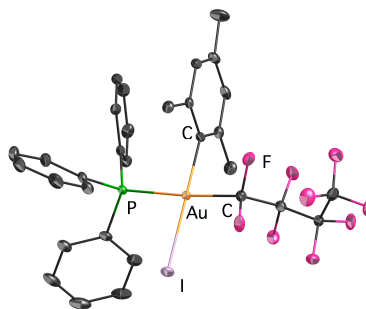
Analogously, the reaction of  $\text{Ph}_3\text{PAuMes}$  with  $i\text{-C}_3\text{F}_7\text{I}$  gave complexes **12**, **4**, and  $\text{Ph}_3\text{PAuI}$ , along with  $\text{MesI}$ , mesitylene and several unidentified organofluorine products (Scheme 3). In contrast with **9** and **10**, complex **12** was always a minor component of the reaction mixture, even at short irradiation times. Nevertheless, **12** could be isolated from the reaction mixture by liquid-diffusion crystallization. Its NMR spectra and crystal structure show that its structure is analogous to that of **9** and **10** (Figure 6). No Au(III) complexes were detected in the reaction of  $\text{Ph}_3\text{PAuMes}$  and  $c\text{-C}_6\text{F}_{11}\text{I}$ , which reacted upon irradiation at 402 nm for 1 min to give **6** and  $\text{MesI}$ .

$\text{IPrAuPh}$  did not react with  $n\text{-C}_4\text{F}_9\text{I}$  or  $i\text{-C}_3\text{F}_7\text{I}$  upon 402 nm irradiation, but it reacted at 310 nm to give  $\text{PhI}$  and complexes **2** or **5**, respectively (Scheme 4; Figures S9 and S10). No Au(III) intermediates were detected in this case.

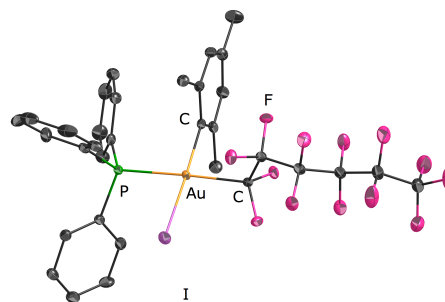


**Scheme 4.** Reactions of  $\text{IPrAuPh}$  with iodoperfluoroalkanes.

The crystal structures of **9**, **10** and **12** (Figures 4, 5 and 6) show slightly distorted square planar coordination geometries, with the  $\text{PPh}_3$  and  $\text{R}_\text{F}$  ligands in a mutual *trans* disposition. The most significant distortion is a widening of the  $\text{I}-\text{Au}-\text{CF}$  angle ( $96.23(6)^\circ$ ) in **12**, probably produced by the steric repulsion between the iodo and perfluoroisopropyl ligands. The  $\text{Au}-\text{CF}_2$  bond distances in the perfluoro-butyl or -hexyl complexes **9** ( $2.110(2)$  Å) and **10** ( $2.118(3)$  Å) are slightly shorter than the  $\text{Au}-\text{CF}$  bond distance in **12** ( $2.152(2)$  Å), and similar to the  $\text{Au}-\text{CF}_2$  bond distance in **1** ( $2.097(2)$  Å).



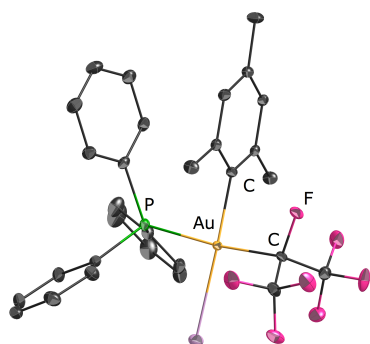
**Figure 4.** Molecular structure of **9** in the solid state (50% thermal ellipsoids). Selected bond lengths and angles:  $\text{Au}-\text{P}$  2.3857(5),  $\text{Au}-\text{CF}_2$  2.110(2),  $\text{Au}-\text{C}_{\text{Mes}}$  2.0659(19),  $\text{Au}-\text{I}$  2.67565(18);  $\text{C}_{\text{Mes}}-\text{Au}-\text{CF}_2$  89.21(8),  $\text{C}_{\text{Mes}}-\text{Au}-\text{P}$  88.39(6),  $\text{CF}_2-\text{Au}-\text{P}$  174.74(6),  $\text{C}_{\text{Mes}}-\text{Au}-\text{I}$  178.53(6),  $\text{CF}_2-\text{Au}-\text{I}$  91.90(6),  $\text{P}-\text{Au}-\text{I}$  90.573(13).



**Figure 5.** Molecular structure of **10** in the solid state (50% thermal ellipsoids). Selected bond lengths and angles:  $\text{Au}-\text{P}$  2.3781(7),  $\text{Au}-\text{CF}_2$  2.118(3),  $\text{Au}-\text{C}_{\text{Mes}}$  2.061(2),  $\text{Au}-\text{I}$  2.6777(3);  $\text{C}_{\text{Mes}}-\text{Au}-\text{CF}_2$  89.10(10),  $\text{C}_{\text{Mes}}-\text{Au}-\text{P}$  90.30(7),  $\text{CF}_2-\text{Au}-\text{P}$  174.95(7),  $\text{C}_{\text{Mes}}-\text{Au}-\text{I}$  175.60(7),  $\text{CF}_2-\text{Au}-\text{I}$  91.65(7),  $\text{P}-\text{Au}-\text{I}$  89.329(18).

In the  $^{19}\text{F}$  NMR spectra of the Au(III) perfluoro-butyl or -hexyl complexes **9**, **10** and **11**, the  $\text{AuCF}_2$  nuclei adjacent to gold resonate at higher  $\delta$  values than those of their Au(I) counterparts **1** or **3** (-79.5 to -81.0 ppm vs. -104 ppm, respectively). The same happens with the perfluoroisopropyl complexes **12** and **4** (-172.1 vs. -199.1 ppm, respectively). In contrast, the  $^{31}\text{P}$  signals of the Au(III) perfluoroalkyls appear at lower  $\delta$  values than those of the Au(I) complexes (23.3–28.3 vs. 38.4–39.6 ppm). The  $^3J_{\text{PF}}$  values of the Au(III) perfluoroalkyl complexes are typically higher than those of their Au(I) counterparts.

The configuration of **11** was assigned on the basis of (i) a lower  $^3J_{\text{PF}}$  value (29.7 Hz) in comparison with **9** and **10** (39.6 and 39.5 Hz), which suggests a mutually *cis* disposition of the triphenylphosphine and perfluorohexyl ligands, and (ii) the coupling between the mesityl aromatic proton and  $^{31}\text{P}$  ( $^5J_{\text{PH}} = 4.1$  Hz), which was not observed in the other complexes and suggests that the triphenylphosphine and mesityl ligands are *trans* to each other.



**Figure 6.** Molecular structure of **12** in the solid state (50% thermal ellipsoids). Selected bond lengths and angles: Au-P 2.3748(6), Au-CF 2.152(2), Au-C<sub>Mes</sub> 2.063(2), Au-I 2.6925(2); C<sub>Mes</sub>-Au-CF 88.46(9), C<sub>Mes</sub>-Au-P 85.91(7), CF-Au-P 172.45(6), C<sub>Mes</sub>-Au-I 173.81(6), CF-Au-I 96.23(6), P-Au-I 89.750(15).

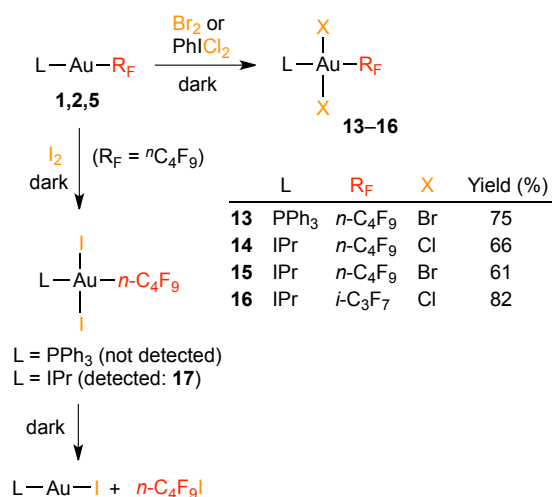
### Reactions of Au(I) perfluoroalkyl complexes with halogens. Reductive elimination reactions from complexes $[\text{Au}(\text{R}_\text{F})\text{X}_2\text{L}]$ (X = Cl, Br, I)

The reaction of **1** with  $\text{Br}_2$  afforded *trans*- $[\text{Au}(n\text{-C}_4\text{F}_9)\text{Br}_2(\text{PPh}_3)]$  (**13**) as the main product (Scheme 5). It was separated from the minor reaction products  $\text{Ph}_3\text{PAuBr}_3$  and  $\text{Ph}_3\text{PAuBr}$  by extraction with *n*-hexane and isolated in a 75% yield. Similarly, complexes **14**, **15** and **16** were isolated in 61–82% yield by reaction of **2** or **5** with  $\text{PhICl}_2$  or  $\text{Br}_2$ . In contrast, **1** reacted with  $\text{PhICl}_2$  to give a mixture containing  $\text{Ph}_3\text{PAuCl}_3$ ,  $\text{Ph}_3\text{PAuCl}$ , and the expected Au(III) perfluoroalkyl complex *trans*- $[\text{Au}(n\text{-C}_4\text{F}_9)\text{Cl}_2(\text{PPh}_3)]$ , which could not be separated. The reactions of **1** or **2** with  $\text{I}_2$  quantitatively gave  $\text{LAuI}$  (L =  $\text{PPh}_3$  or  $\text{IPr}$ ) and  $n\text{-C}_4\text{F}_9\text{I}$  (Scheme 5). The Au(III) complex **17** was observed by NMR spectroscopy at initial stages of the reaction, along with unreacted **2**,  $\text{IPrAuI}$  and  $n\text{-C}_4\text{F}_9\text{I}$  (Figures S11 and S12). The expected Au(III) intermediate of the reaction between **1** and  $\text{I}_2$  was not observed.

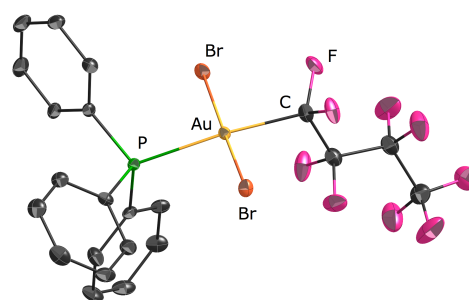
The crystal structure of **13** (Figure 7) shows a slightly distorted square planar *trans* geometry. The unit cell contains two independent molecules with very similar structural

parameters, the main difference between them being the conformational disorder of the perfluorobutyl chain in one of the molecules. The Au–C distances (2.122(4) and 2.123(4) Å) are not significantly different from those of **9** and **10**.

The  $^{31}\text{P}$  NMR signal of **13** appears at a similar  $\delta$  value (27.2 ppm) than for **9–12**. The high value of  $^3J_{\text{PF}}$  (53.4 Hz) is in agreement with the *trans* disposition of the phosphine and the perfluorobutyl ligand. In the  $^{19}\text{F}$  NMR spectra of **13–15**, the  $\delta$  values of the  $\text{AuCF}_2$  appear in the region from -74.1 and -81.9 ppm, which falls in the range observed for the Au(III) perfluorobutyl complexes **9–11**.



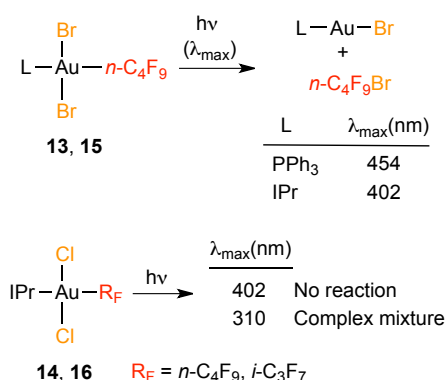
**Scheme 5.** Reactions of Au(I) perfluorobutyl complexes with halogens or  $\text{PhICl}_2$ .



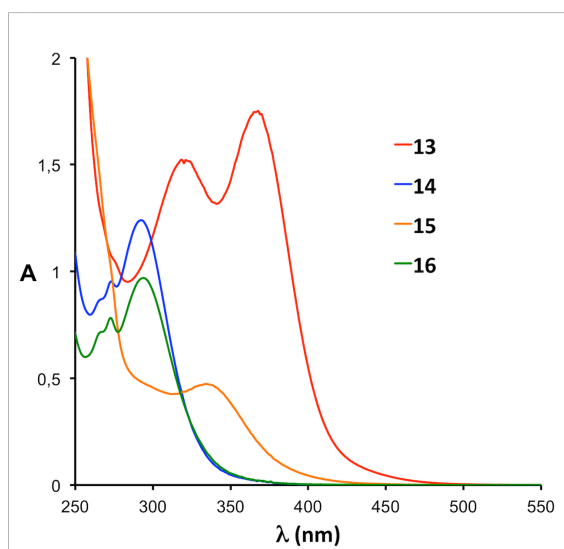
**Figure 7.** Molecular structure of **13** in the solid state (50% thermal ellipsoids). Selected bond lengths and angles: Au-P 2.4019(10), Au-C 2.122(4), Au-Br(1) 2.4237(4), Au-Br(2) 2.4179(4); C-Au-P 176.71(11), C-Au-Br(2) 90.58(11), P-Au-Br(2) 87.13(3), C-Au-Br(1) 90.56(11), P-Au-Br(1) 91.89(3), Br(2)-Au-Br(1) 176.191(15).

Complex **13** underwent reductive elimination of  $n\text{-C}_4\text{F}_9\text{Br}$  when it was exposed to ambient light or irradiated with a blue LED (Scheme 6). In contrast, **15** was stable under blue light, but underwent reductive elimination on irradiation with 402 nm light. This is in agreement with the positions of the absorption bands

in their UV-visible spectra (Figure 8). Thus, the lowest energy absorption maximum of **13** lies at 368 nm, but it tails up to 500 nm, showing a significant absorbance in the visible region. In contrast, the absorption maximum of **15** is at shorter wavelength (335 nm) but presents a low absorbance at 402 nm which decays at longer visible wavelengths. Finally, the lowest energy maxima of **14** and **16** lie at 293 and 294 nm, respectively. These complexes do not significantly absorb beyond 380 nm, therefore they are stable under 402 nm irradiation. However, they decomposed when they were irradiated at 310 nm in an unselective way, to give a mixture of IPrAuCl and several unidentified fluorinated products, among which the chlorofluorocarbons  $n\text{-C}_4\text{F}_9\text{Cl}$ <sup>[22]</sup> or  $i\text{-C}_3\text{F}_7\text{Cl}$ <sup>[23]</sup> were not detected by  $^{19}\text{F}$  NMR (Figures S13–17).



**Scheme 6.** Photoreductive elimination reactions of dihalo perfluoroalkyl Au(III) complexes.



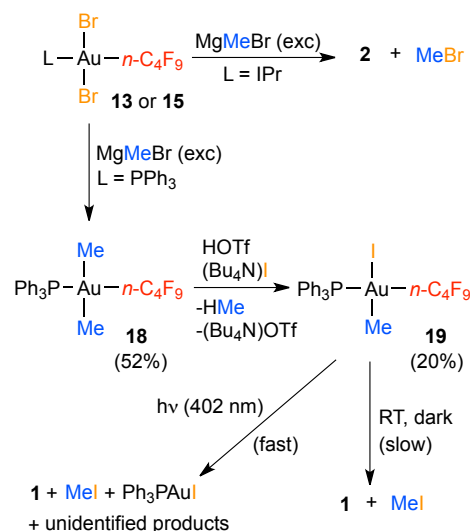
**Figure 8.** UV-vis spectra of complexes **13–16** ( $\text{CH}_2\text{Cl}_2$ ,  $2\text{--}2.3 \times 10^{-4}$  M).

Having Au(III) perfluoroalkyl complexes **13** and **15** in our hands, we attempted to synthesize complexes of the type  $[\text{Au}(n\text{-C}_4\text{F}_9)(\text{Me})(\text{I})\text{L}]$ .

Given that these complexes are potential intermediates in the reaction between  $\text{LAuMe}$  and  $\text{IR}_F$ , their reactivity could provide some insight on the reaction mechanism. First, **13** and **15** were allowed to react with  $\text{MeMgBr}$ , to obtain complexes of the type  $[\text{Au}(n\text{-C}_4\text{F}_9)(\text{Me})(\text{Br})\text{L}]$ , which could subsequently be transformed into the desired iodocomplexes by  $\text{Br}/\text{I}$  metathesis. However, the reaction of **15** with the Grignard reagent (3.8 equiv) in the dark cleanly gave  $\text{MeBr}$  and **2** (Scheme 7; Figure S18). The analogous reaction of **13** with  $\text{MeMgBr}$  (1.2 equiv) gave **1**,  $\text{MeBr}$ ,  $\text{Ph}_3\text{PAuBr}$  and an unidentified product. This suggests that complexes  $[\text{Au}(n\text{-C}_4\text{F}_9)(\text{Me})(\text{Br})\text{L}]$  ( $\text{L} = \text{IPr}, \text{PPh}_3$ ) are unstable at room temperature against reductive elimination of  $\text{MeBr}$ .

In the reaction of **13** with an excess of  $\text{MeMgBr}$ ,  $\text{trans-}[\text{Au}(n\text{-C}_4\text{F}_9)(\text{Me})_2(\text{PPh}_3)]$  (**18**) was the main reaction product. It was isolated in a 52% yield as a white air-stable solid. The presence in its  $^1\text{H}$  NMR spectrum of a unique Au-Me signal integrating for six protons indicated a *trans* configuration. It was stable under 402 nm irradiation but decomposed unselectively upon 310 nm irradiation in  $\text{CD}_2\text{Cl}_2$  solution to give mainly **1**,  $\text{CH}_3\text{CH}_3$ ,  $\text{CDH}_3$  and  $\text{CH}_3\text{CDCl}_2$  (Figure S19).

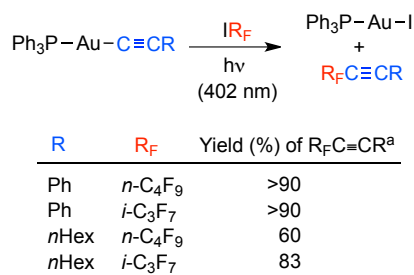
$[\text{Au}(n\text{-C}_4\text{F}_9)(\text{Me})(\text{I})(\text{PPh}_3)]$  (**19**) was obtained by protonolysis of one of the Au-Me bonds of **18** in the presence of  $\text{NBu}_4\text{I}$  (Scheme 7). Formation of  $\text{CH}_4$  was confirmed by carrying out the reaction in an NMR tube in  $\text{CD}_2\text{Cl}_2$ . The  $^3J_{\text{PF}}$  value of **19** (40.5 Hz) suggested a mutual *trans* disposition of the  $\text{PPh}_3$  and  $n\text{-C}_4\text{F}_9$  ligands, and their  $^{31}\text{P}$  and  $^{19}\text{F}$ -Au chemical shift values were comparable to those of **9** and **10**. In the  $^1\text{H}$  NMR spectrum the methylic protons of **19** gave a doublet at 1.78 ppm ( $^3J_{\text{PH}} = 5.6$  Hz). In the dark at room temperature, **19** progressively transformed into **1** and  $\text{MeI}$  over a period of more than 24 h. In contrast, photoirradiation of **19** at 402 nm for 1 min led to almost complete decomposition to  $\text{MeI}$ , **1**,  $\text{Ph}_3\text{PAuI}$  (main products), and several unidentified products (Scheme 7; Figure S20).



**Scheme 7.** Synthesis of Au(III) complexes containing perfluoroalkyl and methyl ligands. Thermal- or photo-reductive elimination reactions of these complexes.

## Reactions of Au(I) alkynyl complexes with iodoperfluorocarbons

The reactions of  $\text{Ph}_3\text{PAuC}\equiv\text{CPh}$  with  $\text{IR}_F$  ( $R_F = n\text{-C}_4\text{F}_9, i\text{-C}_3\text{F}_7$ ) quantitatively gave  $\text{Ph}_3\text{PAuI}$  and alkynes  $R_F\text{C}\equiv\text{CPh}$  (Scheme 8) upon 402 nm irradiation. As in the previous cases, the reaction did not take place in the dark nor at 60 °C ( $\text{CDCl}_3$ , 10 min). Under the same conditions, complex  $\text{Ph}_3\text{PAuC}\equiv\text{C}n\text{Hex}$  reacted with  $\text{IR}_F$  ( $R_F = n\text{-C}_4\text{F}_9, i\text{-C}_3\text{F}_7$ ) to give  $\text{Ph}_3\text{PAuI}$  and alkynes  $R_F\text{C}\equiv\text{C}n\text{Hex}$  as the main products, but complexes **1** or **4** and other unidentified products were also detected by NMR spectroscopy in the reaction mixtures.

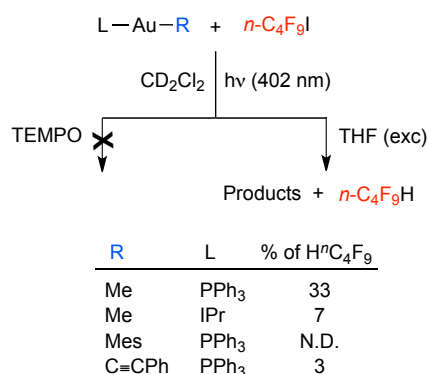


<sup>a</sup> Determined by NMR on the reaction mixture.

**Scheme 8.** Reactions of Au(I) alkynyl complexes with iodoperfluoroalkanes.

## Mechanistic studies

Previous studies have shown that the photooxidative addition of  $\text{ICF}_3$  to Au(I) aryl complexes proceed through a radical chain mechanism which is initiated by the transfer of one electron from the Au(I) complex to an excited molecule of  $\text{ICF}_3$ .<sup>[9c]</sup> In agreement with a radical mechanism, the reactions of  $\text{LAuR}$  ( $L = \text{PPh}_3, R = \text{Me, Mes, C}\equiv\text{CPh}; L = \text{IPr, R} = \text{Me}$ ) and  $\text{IR}_F$  were almost completely inhibited in the presence of the radical trap TEMPO (Scheme 9). In addition, significant amounts of  $n\text{-C}_4\text{F}_9\text{H}$  were formed when the reactions were carried out in presence of an excess of THF (Scheme 9; Figures S21 and S22). This hydrofluorocarbon typically results from  $\alpha$ -hydrogen atom abstraction from THF by a perfluorobutyl radical.<sup>[24]</sup>



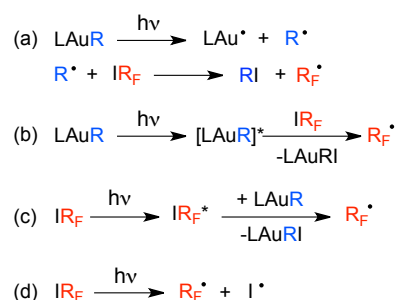
**Scheme 9.** Inhibition by TEMPO and radical-trapping experiments in the reactions of Au(I) organometallic complexes with iodoperfluorobutane.

Since the reactions do not proceed in the dark, perfluoroalkyl radicals could be generated by three possible pathways (Scheme 10): (a) Light-promoted homolysis of the Au–R bond followed by reaction of the generated radicals with  $\text{IR}_F$ ; (b) single electron transfer from an excited  $\text{LAuR}$  complex to a molecule of  $\text{IR}_F$ ; (c) single electron transfer from  $\text{LAuR}$  to an excited molecule of  $\text{IR}_F$ ; (d) light-activated homolysis of the I–R<sub>F</sub> bond.

Homolysis of the Au–R ( $R = \text{Me, Ar}$ ) bond under UV irradiation has been reported,<sup>[18, 25]</sup> however we did not detect the formation of the hydrogen abstraction products HR when  $\text{LAuR}$  ( $L = \text{PPh}_3, R = \text{Me, Mes, C}\equiv\text{CPh}; L = \text{IPr, R} = \text{Me}$ ) and an excess of THF were irradiated with the less energetic 402 nm radiation in  $\text{CD}_2\text{Cl}_2$ . In contrast, decreasing the wavelength to 310 nm induced formation of HR for complexes  $\text{Ph}_3\text{PAuR}$  ( $R = \text{Me}$  or  $\text{Mes}$ ) but not for  $R = \text{C}\equiv\text{CPh}$  (Figures S23 and S24). Thus, pathway (a) was discarded.

Pathway (b) requires previous photoexcitation of the Au(I) complex. The emission band of the used LED has its maximum at 402 nm and the high-energy onset at ca. 370 nm. Since the absorbance of complexes  $\text{LAuMe}$  ( $L = \text{PPh}_3, \text{IPr}$ ) at wavelengths longer than 350 nm is zero, these complexes can not be excited upon irradiation with the 402 nm LED (Figure S25). In contrast,  $\text{Ph}_3\text{PAuMes}$  and  $\text{Ph}_3\text{PAuC}\equiv\text{CPh}$  show a significant absorbance in the LED emission range. Remarkably,  $\text{IPrAuPh}$  does not react with  $\text{IR}_F$  ( $R_F = n\text{-C}_4\text{F}_9, i\text{-C}_3\text{F}_7$ ) upon irradiation at 402 nm, despite its absorbance at this wavelength is higher than that of  $\text{IPrAuMe}$ .

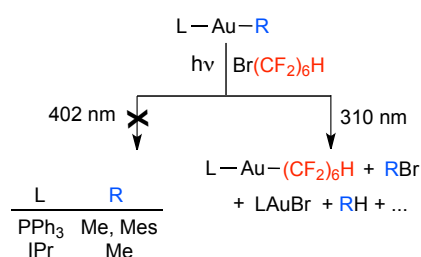
Pathways (c) and (d) require previous photoexcitation of the iodoperfluoroalkane. The absorption maxima of  $\text{IR}_F$  lie at 269 nm ( $R_F = n\text{-C}_4\text{F}_9$ ) and 272 nm ( $R_F = i\text{-C}_3\text{F}_7$ ), but the bands tail up to ca. 375 nm (Figure S25). Since the overlap between the LED emission and the  $\text{IR}_F$  absorption bands is minimal, the number of excited molecules in these conditions should be very small. Accordingly, attempts to trap possible perfluoroalkyl radicals formed by I–C homolysis by irradiating  $\text{CD}_2\text{Cl}_2$  solutions of  $n\text{-C}_4\text{F}_9\text{I}$  in the presence of THF or norbornene at 402 nm were unsuccessful. Neither the THF  $\alpha$ -hydrogen abstraction product ( $n\text{-C}_4\text{F}_9\text{H}$ ), nor the product resulting from  $n\text{-C}_4\text{F}_9\text{I}$  addition to the norbornene C=C bond were detected by NMR. This suggests that in the absence of the Au(I) complexes the extent of I–C homolysis is insignificant and disfavours pathway (d).



**Scheme 10.** Pathways for the generation of perfluoroalkyl radicals in the photochemical reactions of Au(I) organometallic complexes with iodoperfluoroalkanes.

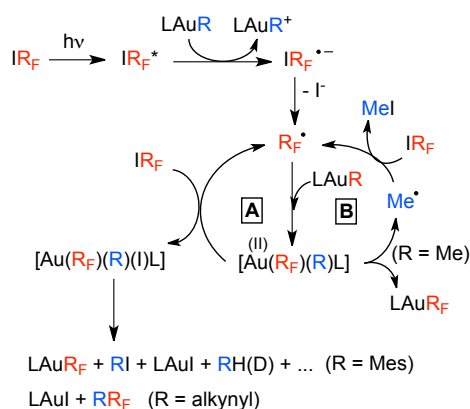


To get further evidence on the initiation mechanism, we investigated the reactions of complexes LAuR (L = Ph<sub>3</sub>P, R = Me, Mes, C≡CR; L = IPr, R = Me) with Br(CF<sub>2</sub>)<sub>6</sub>H, which absorbs at lower wavelengths ( $\lambda_{\text{max}} < 200$  nm) and thus can not be excited by the 402 nm LED (Scheme 11). No reaction was observed in any case with this light source, suggesting that excitation of the halocarbon is necessary for the initiation of the reaction. In contrast, irradiation at 310 nm produced mixtures containing mainly LAu(CF<sub>2</sub>)<sub>6</sub>H and RBr in all cases,<sup>[26]</sup> except for Ph<sub>3</sub>PAuC≡CR, which did not react (Figures S26–S33). Since UV light is able to promote homolysis of the Au–R (R = Me, Ar) bond,<sup>[18, 25]</sup> this process could trigger the reactions with Br(CF<sub>2</sub>)<sub>6</sub>H. The lack of reactivity of Ph<sub>3</sub>PAuC<sub>6</sub>F<sub>5</sub> against *i*-C<sub>3</sub>F<sub>7</sub>I under irradiation at 402 is also in line with pathway (c),<sup>[27]</sup> considering its lower reducing power in comparison with Ph<sub>3</sub>PAuR (R = Me, Mes or C=CPh).



**Scheme 11.** Reactions of Au(I) organometallic complexes with 1-bromo-6-H-perfluorohexane upon irradiation at different wavelengths.

In summary, the available evidence points to (c) being the dominant initiation pathway under irradiation at 402 nm. Some of the excited IR<sub>F</sub> molecules could accept one electron from a Au(I) complex to give I<sup>•</sup> and a perfluoroalkyl radical that would initiate a radical chain reaction. Addition of the radical to a LAuR molecule would give a perfluoroalkyl Au(II) intermediate, which would react with IR<sub>F</sub> to give a Au(III) complex and another perfluoroalkyl radical, which would repeat the process (Scheme 12, pathway A).

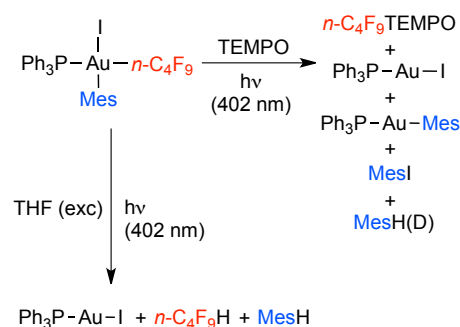


**Scheme 12.** Proposed radical chain mechanism for the reactions of Au(I) organometallic complexes with iodoperfluoroalkanes.

Complexes [Au(R<sub>F</sub>)Me(I)L] (L = IPr or PPh<sub>3</sub>) were not observed in the reaction mixtures, but one of these potential intermediates (**19**, L = PPh<sub>3</sub>) was prepared by an alternative route. As expected, **19** is unstable against reductive elimination of MeI, being the photochemical decomposition much faster than the thermal one. However, photodecomposition of **19** gave MeI and **1**, along with Ph<sub>3</sub>PAuI and several unidentified products (Figure S20). Since the reaction of Ph<sub>3</sub>PAuMe and I<sup>n</sup>C<sub>4</sub>F<sub>9</sub> cleanly affords MeI and **1**, a pathway not involving an intermediate of the type [Au(R<sub>F</sub>)(R)(I)L] could be operative. As an alternative, we propose pathway **B** (Scheme 12), where homolysis of the Au(II) intermediate [Au(R<sub>F</sub>)(R)L] would give LAuR<sub>F</sub> and a methyl radical, which would react with IR<sub>F</sub> to generate MeI and a perfluoroalkyl radical. A similar pathway has been previously proposed to explain the radical reactions of LAuMe (L = PMe<sub>3</sub>, PMe<sub>2</sub>Ph, PMePh<sub>2</sub>, PPh<sub>3</sub>) with ICF<sub>3</sub><sup>[16]</sup> or PhSH,<sup>[28]</sup> and the reaction of Ph<sub>3</sub>PAuMe with [OsH<sub>2</sub>(CO)<sub>4</sub>].<sup>[29]</sup> In agreement with this pathway, small amounts of MeH or the adduct Me–TEMPO were detected by NMR spectroscopy when the reactions of Ph<sub>3</sub>PAuMe and *n*-C<sub>4</sub>F<sub>9</sub>I were carried out in the presence of THF or TEMPO under 402 nm irradiation (Figures S21 and S22). These products were not detected in the absence of the iodoperfluoroalkane.

When L = PPh<sub>3</sub>, R = Mes and R<sub>F</sub> is a primary perfluoroalkyl, the Au(III) intermediates [Au(R<sub>F</sub>)(Mes)I(PPh<sub>3</sub>)] are stable enough to be isolated. In contrast, when R<sub>F</sub> is a secondary perfluoroalkyl the Au(III) intermediate was observed in low concentration (R<sub>F</sub> = *i*-C<sub>3</sub>F<sub>7</sub>), or it was not detected (R<sub>F</sub> = *c*-C<sub>6</sub>F<sub>11</sub>). This suggests that bulkier perfluoroalkyl ligands could destabilize the Au(III) complexes.

Complexes [Au(R<sub>F</sub>)(Mes)I(PPh<sub>3</sub>)] are stable at room temperature but under 402 nm irradiation they decompose to give Ph<sub>3</sub>PAuR<sub>F</sub>, MeI, Ph<sub>3</sub>PAuI, mesitylene and several unidentified organofluorine products. Formation of *n*-C<sub>4</sub>F<sub>9</sub>TEMPO or *n*-C<sub>4</sub>F<sub>9</sub>H when [Au(*n*-C<sub>4</sub>F<sub>9</sub>)(Mes)I(PPh<sub>3</sub>)] was irradiated in the presence of TEMPO or THF (Scheme 13, figures S34 and S35) suggests that this decomposition takes place through a radical mechanism. Remarkably, this photodecomposition process has not been reported for the trifluoromethylated analogues [Au(CF<sub>3</sub>)(Ar)I(PPh<sub>3</sub>)].<sup>[9c]</sup>



**Scheme 13.** Perfluorobutyl radical trapping experiments in the photodecomposition of Au(III) perfluorobutyl complex **9**.

## Conclusions

The reactions of LAuR (L = PPh<sub>3</sub>, IPr; R = methyl, mesityl or alkynyl) with primary or secondary perfluoroalkyl iodides proceed upon irradiation with a mild light source (402 nm) and follow a photoinitiated radical mechanism. They afford Au(I) or Au(III) perfluoroalkyl complexes of the types LAuR<sub>F</sub> or [Au(R<sub>F</sub>)(R)I(PPh<sub>3</sub>)], or alkynes R<sub>F</sub>C≡CR, depending on the nature of L, R and R<sub>F</sub>.

Whereas oxidative addition complexes of the type [Au(R<sub>F</sub>)(R)I(PPh<sub>3</sub>)] were isolated for L = PPh<sub>3</sub> and R = Mes, they were not detected in the reactions of LAuMe and IR<sub>F</sub>. Evidence for different radical pathways in these reactions was obtained.

Au(III) perfluoroalkyl complexes of the type *trans*-[Au(R<sub>F</sub>)X<sub>2</sub>L] (L = PPh<sub>3</sub>, IPr) have been prepared by oxidation of LAuR<sub>F</sub> with PhICl<sub>2</sub> or Br<sub>2</sub>. These complexes are light-sensitive and undergo reductive elimination of XR<sub>F</sub> under photoirradiation. In contrast, their diiodo analogues (X = I) are thermally unstable and could not be isolated.

The photoinstability of Au(III) perfluoroalkyl complexes contrasts with the reported stability of their trifluoromethyl counterparts,<sup>[9c]</sup> and should be taken into account when designing gold-catalysed perfluoroalkylation reactions.

The first gold complexes containing perfluoroalkyl ligands other than trifluoromethyl have been isolated and structurally characterized. These include the first perfluorocyclohexyl transition metal complexes reported. Studies on the reactivity and stability of Au(III) perfluoroalkyl complexes containing different types of ligands are underway and will be reported in due course.

## Experimental Section

**General considerations and materials:** Ph<sub>3</sub>PAuMe<sup>[30]</sup> and IPrAuMe<sup>[31]</sup> were prepared by modified literature methods (see Supporting Information). Ph<sub>3</sub>PAuMes,<sup>[32]</sup> IPrAuBu,<sup>[31]</sup> IPrAuPh,<sup>[33]</sup> Ph<sub>3</sub>PAuC≡CPh<sup>[34]</sup> and Ph<sub>3</sub>PAuC≡CnHex<sup>[35]</sup> were prepared as previously reported. Reactions were carried out under a N<sub>2</sub> atmosphere by using standard Schlenk techniques. Inhibitor-free CH<sub>2</sub>Cl<sub>2</sub> (Fisher) or CD<sub>2</sub>Cl<sub>2</sub> (Eurisotop) were used as solvents in preparative or NMR-tube reactions. Both were passed through an activated basic alumina column, degassed by N<sub>2</sub> bubbling, and stored over 4 Å molecular sieves in a N<sub>2</sub> atmosphere and protected of light. Unless otherwise stated, the complexes were isolated in an air atmosphere using commercial solvents (HPLC or analytical grade). Irradiations were performed using a blacklight or blue LED stripe (λ<sub>max</sub> = 402 or 454 nm, respectively; 6 W, 1 m length) or a fluorescent lamp (λ<sub>max</sub> = 310 nm, 36 W). The LED stripes were placed in a reflecting metal can around the reaction tube. NMR spectra were measured on Bruker Avance 200, 300, 400 or 600 MHz spectrometers. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced on the solvent signals.<sup>[36]</sup> <sup>19</sup>F and <sup>31</sup>P{<sup>1</sup>H} spectra were referenced against external CFCl<sub>3</sub> or H<sub>3</sub>PO<sub>4</sub>, respectively. GC-MS analyses were performed on an Agilent 6890 gas chromatograph with a HP5 column coupled to an Agilent 5973 mass spectrometer, which was equipped with an electron impact or chemical ionization (CH<sub>4</sub> as reagent gas) ion source. Elemental analyses were carried out with a LECO CHNS-932 microanalyzer. UV-vis absorption spectra were recorded on a Perkin-Elmer Lambda 750S spectrometer using 10 mm quartz cells and spectroscopic grade solvents. Infrared spectra were recorded in the range 4000–200 cm<sup>-1</sup> on a Perkin-Elmer 16F PC FT-IR

spectrometer with nujol mulls between polyethylene sheets. Melting points were determined on a Reichert apparatus in an air atmosphere.

**Ph<sub>3</sub>PAu(*n*-C<sub>4</sub>F<sub>9</sub>) (1).** *n*-C<sub>4</sub>F<sub>9</sub>I (24 μL, 0.14 mmol) was added to a solution of Ph<sub>3</sub>PAuMe (61 mg, 0.13 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) in a Schlenk tube. The solution was irradiated at 402 nm for 5 min with stirring and evaporated to dryness under vacuum. Addition of *n*-pentane (1 mL) gave a suspension which was filtered. The white solid was washed with cold *n*-pentane (2 × 1 mL, 0 °C) and air dried. Yield: 82 mg (0.12 mmol), 94%. M.p. 104–107 °C (dec); <sup>1</sup>H NMR (300.1 MHz, CDCl<sub>3</sub>): δ=7.55–7.46 (m, 15H); <sup>13</sup>C NMR (75.5 MHz, CDCl<sub>3</sub>): δ=134.3 (d, J<sub>P,C</sub>=13.6 Hz, Ph), 131.9 (d, J<sub>P,C</sub>=2.0 Hz, Ph), 129.5 (d, J<sub>P,C</sub>=11.3 Hz, Ph), 129.2 (d, J<sub>P,C</sub>=54.6 Hz, C-P), 120.4–109.4 (several m; C-F); <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>): δ=-81.3 (tt, 3F, J<sub>F,F</sub> = 9.5 and 3.2 Hz; CF<sub>3</sub>), -104.5 (m, 2F; AuCF<sub>2</sub>), -120.6 (m, 2F), -125.5 (m, 2F); <sup>31</sup>P (121.5 MHz, CDCl<sub>3</sub>): δ=38.8 (tt, <sup>3</sup>J<sub>P,F</sub> = 23.1 Hz, <sup>4</sup>J<sub>P,F</sub> = 1.7 Hz); IR (Nujol):  $\tilde{\nu}$  1344, 1273, 1233, 1189, 1172, 1146, 1022, 1067, 999 cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>22</sub>H<sub>15</sub>AuF<sub>9</sub>P: C 38.96, H 2.23; found: C, 38.93, H 2.16.

**IPrAu(*n*-C<sub>4</sub>F<sub>9</sub>) (2).** It was prepared in the same way as for **1** from IPrAuMe (191 mg, 0.318 mmol) and *n*-C<sub>4</sub>F<sub>9</sub>I (67 μL, 0.38 mmol). The irradiation time was 8 min. *n*-Hexane (5 mL) was added to the solution and it was concentrated under vacuum until a white solid precipitated. The suspension was filtered and the solid was washed with *n*-hexane (2 × 1 mL) and air dried. Yield: 195 mg (0.242 mmol), 76%. M.p. 185–187 °C; <sup>1</sup>H NMR (400.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=7.54 (t, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.34 (d, <sup>3</sup>J<sub>H,H</sub> = 7.8 Hz, 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.23 (s, 2H, HC=CH), 2.55 (sept, J<sub>H,H</sub> = 6.9 Hz, 4H, CHMe<sub>2</sub>), 1.32 (d, J<sub>H,H</sub> = 6.9 Hz, 12H, Me), 1.23 (d, J<sub>H,H</sub> = 6.9 Hz, 12H, Me); <sup>13</sup>C NMR (100.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=189.0 (t, <sup>3</sup>J<sub>F,C</sub> = 6.5 Hz, N<sub>2</sub>CAu), 150.0 (tt, <sup>1</sup>J<sub>F,C</sub> = 285.4, <sup>2</sup>J<sub>F,C</sub> = 47.0 Hz, AuCF<sub>2</sub>), 146.1 (s, Ar), 134.2 (s, Ar), 130.9 (s, Ar), 124.4 (s, Ar), 124.0 (s, CH=CH), 119.9–109.6 (several m, C-F), 29.2 (s, CH), 24.3 (s, Me), 24.1 (s, Me); <sup>19</sup>F (188.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=-82.1 (tt, J<sub>F,F</sub> = 9.4 and 3.5 Hz, 3F, CF<sub>3</sub>), -106.3 (m, 2F, AuCF<sub>2</sub>), -123.3 (q, J<sub>F,F</sub> = 9.2 Hz, 2F), -126.1 (t, J<sub>F,F</sub> = 11.2 Hz, 2F); IR (Nujol):  $\tilde{\nu}$  1227, 1192 cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>31</sub>H<sub>36</sub>F<sub>9</sub>AuN<sub>2</sub>: C 46.28, H 4.51, N 3.48; found: C 46.37, H 4.50, N 3.35.

**Ph<sub>3</sub>PAu(*n*-C<sub>6</sub>F<sub>13</sub>) (3).** *n*-C<sub>6</sub>F<sub>13</sub>I (104 μL, 0.468 mmol) was added to a solution of Ph<sub>3</sub>PAuMe (111 mg, 0.234 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) in a Schlenk tube. The solution was irradiated at 402 nm at room temperature for 10 min with stirring. The reaction mixture was filtered through a PTFE syringe filter to remove a small amount of gold particles, and the filtrate was evaporated to dryness under vacuum to give a colourless oil which was soluble in *n*-pentane. Yield: 163 mg (0.209 mmol), 90%. Satisfactory elemental analyses could not be obtained because of the air sensitivity of the oil. <sup>1</sup>H NMR (200.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=7.59–7.46 (m, 15H); <sup>13</sup>C NMR (100.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=134.6 (d, J<sub>P,C</sub> = 13.5 Hz, Ph), 132.2 (d, J<sub>P,C</sub> = 2 Hz, Ph), 129.7 (d, J<sub>P,C</sub> = 11.2 Hz, Ph), 129.4 (d, J<sub>P,C</sub> = 55.3 Hz, C-P), 119.2–108.5 (several m, C-F); <sup>19</sup>F NMR (188.3 MHz, CDCl<sub>3</sub>): δ=-81.3 (t, J<sub>F,F</sub> = 9.6 Hz, 3F, CF<sub>3</sub>), -104.3 (m, 2F, AuCF<sub>2</sub>), -119.7 (m, 2F), -121.7 (m, 2F), -123.2 (m, 2F), -126.6 (m, 2F); <sup>31</sup>P (162.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=38.6 (t, <sup>3</sup>J<sub>P,F</sub> = 22.6 Hz).

**Ph<sub>3</sub>PAu(*i*-C<sub>3</sub>F<sub>7</sub>) (4).** It was prepared in the same way as for **1** from *i*-C<sub>3</sub>F<sub>7</sub>I (16 μL, 0.11 mmol) and Ph<sub>3</sub>PAuMe (50 mg, 0.11 mmol). White solid. Yield: 50 mg (0.080 mmol), 75%. M.p. 156 °C (dec); <sup>1</sup>H NMR (400.9 MHz, CDCl<sub>3</sub>): δ=7.56–7.49 (m, 15H); <sup>13</sup>C NMR (100.8 MHz, CDCl<sub>3</sub>): δ=134.3 (d, J<sub>P,C</sub> = 13.1 Hz, Ph), 132.0 (d, J<sub>P,C</sub> = 1.9 Hz, Ph), 129.5 (d, J<sub>P,C</sub> = 11.3 Hz, Ph), 129.1 (d, J<sub>P,C</sub> = 56.1 Hz, C-P); the C-F signals were not observed; <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>): δ=-69.3 (dd, <sup>3</sup>J<sub>F,F</sub> = 12.4 Hz, <sup>4</sup>J<sub>P,F</sub> = 4.5 Hz, 6F, CF<sub>3</sub>), -199.1 (d of septets, <sup>3</sup>J<sub>P,F</sub> = 12.1 Hz, 1F, CF); <sup>31</sup>P (162.3 MHz, CDCl<sub>3</sub>): δ=39.6 (d of septets, <sup>3</sup>J<sub>P,F</sub> = 12.1 Hz, <sup>4</sup>J<sub>P,F</sub> = 3.9 Hz); IR (Nujol):  $\tilde{\nu}$  1301, 1271, 1204, 1175, 1030 cm<sup>-1</sup>

(CF); elemental analysis calcd (%) for  $C_{21}H_{15}AuF_7P$ : C 40.15, H 2.41; found: C 40.02, H 2.43.

**IPrAu(*i*-C<sub>3</sub>F<sub>7</sub>) (5).** It was prepared in the same way as for **1** from IPrAuMe (102 mg, 0.170 mmol) and *i*-C<sub>3</sub>F<sub>7</sub>I (29  $\mu$ L, 0.21 mmol). The irradiation time was 8 min. The volatiles were removed under vacuum and the solid was stirred with *n*-pentane (1 mL), separated by filtration and air dried. Yield: 66 mg (0.087 mmol), 51%. M.p. 243–245 °C; <sup>1</sup>H NMR (400.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =7.54 (t,  $J_{H,H}$  = 7.8 Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.32 (d,  $J_{H,H}$  = 7.8 Hz, 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.24 (s, 2H, CH=CH), 2.52 (sept,  $J_{H,H}$  = 6.9 Hz, 4H, CHMe<sub>2</sub>), 1.29 (d,  $J_{H,H}$  = 6.9 Hz, 12H, Me), 1.23 (d,  $J_{H,H}$  = 6.9 Hz, 12H, Me); <sup>13</sup>C NMR (100.8 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =188.0 (s, N<sub>2</sub>CAu), 146.2 (s, Ar), 134.2 (s, Ar), 130.8 (s, Ar), 124.3 (s, Ar), 123.8 (s, CH=CH), 29.1 (s, CH), 24.2 (s, Me), 24.1 (s, Me); the C-F signals were not observed; <sup>19</sup>F NMR (188.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =-70.9 (d, <sup>3</sup> $J_{F,F}$  = 11.7 Hz, 6F, CF<sub>3</sub>), -203.2 (sept, <sup>3</sup> $J_{F,F}$  = 12.5 Hz, 1F, CF); IR (Nujol):  $\tilde{\nu}$  1299, 1272, 1199, 1175 cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>30</sub>H<sub>36</sub>F<sub>7</sub>AuN<sub>2</sub>: C 47.75, H 4.81, N 3.71; found: C 47.56, H 4.74, N 3.60.

**Ph<sub>3</sub>PAu(c-C<sub>6</sub>F<sub>11</sub>) (6).** It was prepared in the same way as for **1** from c-C<sub>6</sub>F<sub>11</sub>I (45  $\mu$ L, 0.24 mmol) and Ph<sub>3</sub>PAuMe (103 mg, 0.217 mmol). The reaction mixture was concentrated under vacuum up to ca. 0.5 mL and dry *n*-pentane (3 mL) was added with stirring. The resulting precipitate was allowed to sediment and the mother liquor was removed with a pipette under a N<sub>2</sub> atmosphere. The white solid was washed in the same way with dry *n*-pentane (2  $\times$  1 mL) and dried under vacuum. Yield: 115 mg (0.155 mmol), 72%. M.p. 130 °C (dec); <sup>1</sup>H NMR (200.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =7.56–7.48 (m, 15 H, Ph); <sup>13</sup>C NMR (50.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C):  $\delta$ =134.5 (d,  $J_{P,C}$  = 13.7 Hz, Ph), 132.3 (d,  $J_{P,C}$  = 2.1 Hz, Ph), 129.7 (d,  $J_{P,C}$  = 11.4 Hz, Ph), 129.2 (d,  $J_{P,C}$  = 56.7 Hz, C-P); the C-F signals were not observed; <sup>19</sup>F NMR (188.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C):  $\delta$ =-109.2 (d, <sup>2</sup> $J_{F,F}$  = 269.3 Hz, 2F), -118.8 (d, <sup>2</sup> $J_{F,F}$  = 280.5 Hz, 2F), -129.6 (br m, 5F), -138.2 (br m, 1F), -206.0 (br s, 1F, AuCF); <sup>19</sup>F (564.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -60 °C): (signals of the major conformer)  $\delta$ =-108.5 (d, <sup>2</sup> $J_{F,F}$  = 292.9 Hz, 2F), -117.7 (d, <sup>2</sup> $J_{F,F}$  = 293.0 Hz, 2F), -123.2 (two overlapped d, <sup>2</sup> $J_{F,F}$  = 279.9 Hz, 3F), -135.7 (d, <sup>2</sup> $J_{F,F}$  = 277.6 Hz, 2F), -143.0 (d, <sup>2</sup> $J_{F,F}$  = 282.4 Hz, 1F), -200.0 (s, 1F, AuCF); (signals of the minor conformer)  $\delta$ =-111.9 (d, <sup>2</sup> $J_{F,F}$  = 254.7 Hz, 2F), -113.3 (d, <sup>2</sup> $J_{F,F}$  = 275.8 Hz, 2F), -119.7 (d, <sup>2</sup> $J_{F,F}$  = 255.3 Hz, 2F), -123.7 (d, <sup>2</sup> $J_{F,F}$  = 316.7 Hz, 1F), -140.7 (d, <sup>2</sup> $J_{F,F}$  = 280.3 Hz, 1F), -142.1 (d, <sup>2</sup> $J_{F,F}$  = 275.5 Hz, 2F), -219.7 (s, 1F, AuCF); <sup>19</sup>F NMR (188.3 MHz, CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>, 80 °C):  $\delta$ =-108.6 (d, <sup>2</sup> $J_{F,F}$  = 280.4 Hz, 2F), -117.8 (d, <sup>2</sup> $J_{F,F}$  = 283.2 Hz, 2F), -128.4 (d, <sup>2</sup> $J_{F,F}$  = 273.7 Hz, 1F), -128.7 (br s, 4F), -137.1 (d, <sup>2</sup> $J_{F,F}$  = 280.4 Hz, 1F), -204.8 (s, 1F, AuCF); <sup>31</sup>P (242.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$ =39.4 (br m); <sup>31</sup>P (242.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, -60 °C):  $\delta$ =39.1 (br m, major conformer), 37.7 (br m, minor conformer); IR (Nujol, cm<sup>-1</sup>):  $\tilde{\nu}$  1246, 1227, 1216, 1197, 1164, 1130, 1039, 1002, cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>24</sub>H<sub>15</sub>AuF<sub>11</sub>P: C 38.94, H 2.04; found: C 39.03, H 2.03.

**IPrAu(c-C<sub>6</sub>F<sub>11</sub>) (7).** It was prepared in the same way as for **1** from IPrAuMe (130 mg, 0.216 mmol) and c-C<sub>6</sub>F<sub>11</sub>I (46  $\mu$ L, 0.24 mmol). The irradiation time was 15 min. The reaction mixture was evaporated to dryness. The residue was extracted with *n*-hexane (20 mL). The extract was concentrated and chromatographed in a silicagel column. Elution with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:1) gave pure **7** ( $R_f$  = 0.6), which was obtained after evaporation as a white solid. Yield: 112 mg (0.151 mmol), 70.0%. M.p. 225–226 °C; <sup>1</sup>H NMR (200.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 21 °C):  $\delta$ =7.54 (t,  $J_{H,H}$  = 7.8 Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.33 (d,  $J_{H,H}$  = 7.8 Hz, 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.26 (s, 2H, CH=CH), 2.55 (sept,  $J_{H,H}$  = 6.9 Hz, 4H, CHMe<sub>2</sub>), 1.31 (d,  $J_{H,H}$  = 6.9 Hz, 12H, Me), 1.24 (d,  $J_{H,H}$  = 6.9 Hz, 12H, Me); <sup>13</sup>C (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 25 °C):  $\delta$ =188.1 (s, N<sub>2</sub>CAu), 146.2 (s, Ar), 134.2 (s, Ar), 130.9 (s, Ar), 124.4 (s, Ar), 123.9 (s, CH=CH), 29.22 (s, CH), 24.21 (s, Me), 24.17 (s, Me); the C-F signals were not observed; <sup>19</sup>F (564.6 MHz, CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>, -60 °C): (signals of the major conformer)  $\delta$ =-108.4 (d, <sup>2</sup> $J_{F,F}$  = 293.1 Hz, 2F), -117.3 (d, <sup>2</sup> $J_{F,F}$  = 292.7 Hz, 2F), -122.1 (d, <sup>2</sup> $J_{F,F}$  = 276.4 Hz, 2F), -122.3 (d, <sup>2</sup> $J_{F,F}$

= 283.6 Hz, 1F), -135.1 (d, <sup>2</sup> $J_{F,F}$  = 275.6 Hz, 2F), -142.4 (d, <sup>2</sup> $J_{F,F}$  = 281.8 Hz, 1F), -201.7 (m, 1F, AuCF); (signals of the minor conformer)  $\delta$ =-111.3 (d, <sup>2</sup> $J_{F,F}$  = 248.9 Hz, 2F), -112.8 (d, <sup>2</sup> $J_{F,F}$  = 272.5 Hz, 2F), -118.8 (d, <sup>2</sup> $J_{F,F}$  = 255 Hz, 2F), -122.8 (d, <sup>2</sup> $J_{F,F}$  = 299.7 Hz, 1F), -140.7 (d, <sup>2</sup> $J_{F,F}$  = 281.3 Hz, 1F), -141.3 (d, <sup>2</sup> $J_{F,F}$  = 271.8 Hz, 2F), -219.0 (s, 1F, AuCF); <sup>19</sup>F (564.6 MHz, CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>, 23 °C):  $\delta$ =-109.2 (d, <sup>2</sup> $J_{F,F}$  = 279.8 Hz, 2F), -118.1 (d, <sup>2</sup> $J_{F,F}$  = 282.1 Hz, 2F), from -125 to -140 (very br m, 6F), -204.6 (very br, 1F, AuCF); <sup>19</sup>F (564.6 MHz, CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>, 95 °C):  $\delta$ =-109.0 (d, <sup>2</sup> $J_{F,F}$  = 280.7 Hz, 2F), -118.1 (d, <sup>2</sup> $J_{F,F}$  = 283.4 Hz, 2F), -128.1 (m, 5F), -137.0 (d, <sup>2</sup> $J_{F,F}$  = 274.2 Hz, 1F), -206.7 (s, 1F, AuCF); IR (Nujol):  $\tilde{\nu}$  1192, 1003 cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>33</sub>H<sub>36</sub>F<sub>11</sub>AuN<sub>2</sub>: C 45.74, H 4.19, N 3.23; found: C 45.79, H 4.08, N 3.10.

**Reaction of Ph<sub>3</sub>PAuMe with C<sub>6</sub>F<sub>5</sub>CF<sub>2</sub>I. NMR data of Ph<sub>3</sub>PAu(CF<sub>2</sub>C<sub>6</sub>F<sub>5</sub>) (8).** C<sub>6</sub>F<sub>5</sub>CF<sub>2</sub>I (4  $\mu$ L, 0.02 mmol) was added to a solution of Ph<sub>3</sub>PAuMe (9.5 mg, 0.020 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) in a NMR tube. After 40 min in the dark, the NMR spectra of the mixture showed quantitative formation of **8** and Mel. The same reaction was carried out in a larger scale in CH<sub>2</sub>Cl<sub>2</sub> to isolate **8**. However, when the reaction mixture was evaporated under vacuum and *n*-pentane was added to precipitate **8**, partial decomposition to metallic gold took place and a grey oil was formed. This oil was a mixture containing **8** and several unidentified compounds. NMR data of **8**: <sup>1</sup>H NMR (200.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =7.57–7.46 (m, 15 H); <sup>19</sup>F NMR (188.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =-80.7 (qd, <sup>4</sup> $J_{F,F}$  = <sup>3</sup> $J_{P,F}$  = 25.4 Hz, <sup>6</sup> $J_{F,F}$  = 3.0 Hz, 2F, CF<sub>2</sub>), -143.4 (m, 2F), -157.8 (t,  $J_{F,F}$  = 21.1 Hz, 1F), -163.8 (m, 2F); <sup>31</sup>P (81.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =38.4 (t, <sup>3</sup> $J_{P,F}$  = 26.4 Hz).

**SP-4-4-[Au(*n*-C<sub>4</sub>F<sub>9</sub>)(Mes)](PPh<sub>3</sub>) (9).** *n*-C<sub>4</sub>F<sub>9</sub>I (91  $\mu$ L, 0.53 mmol) was added to a solution of [Au(Mes)(PPh<sub>3</sub>)] (102 mg, 0.176 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The solution was irradiated at 402 nm for 80 s at room temperature with stirring. The resulting yellow solution was evaporated to dryness under vacuum. The residue was stirred with *n*-pentane (10 mL) to give a pale yellow precipitate, which was isolated by filtration, washed with *n*-pentane (3  $\times$  2 mL) and air dried. Yield: 102 mg (0.110 mmol), 63%. M.p. 160–165 °C; <sup>1</sup>H NMR (600.1 MHz, CDCl<sub>3</sub>):  $\delta$ =7.49–7.32 (m, 15H, Ph), 6.34 (s, 2H, H<sub>3</sub>, Mes), 2.12 (s, 6H, Me), 2.08 (s, 3H, Me); <sup>13</sup>C NMR (150.9 MHz, CDCl<sub>3</sub>):  $\delta$ =149.9 (m, C1, Mes), 136.5 (s, Mes), 136.2 (s, Mes), 135.0 (d,  $J_{P,C}$  = 9.2 Hz, Ph), 131.8 (s, Ph), 129.5 (s, Mes), 128.5 (d,  $J_{P,C}$  = 11.2 Hz, Ph), 127.2 (d,  $J_{P,C}$  = 56.8 Hz, C-P), 120.8–109.6 (several m, C-F), 23.6 (s, Me), 20.3 (s, Me); <sup>19</sup>F NMR (188.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =-80.4 (dtm,  $J_{F,F}$  = 15.6 Hz, <sup>3</sup> $J_{P,C}$  = 39.4 Hz, AuCF<sub>2</sub>), -81.7 (tt,  $J_{F,F}$  = 10.1 and 2.9 Hz, CF<sub>3</sub>), -112.8 (m, 2F), -126.6 (m, 2F); <sup>31</sup>P NMR (81.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =23.3 (t, <sup>3</sup> $J_{P,F}$  = 39.6 Hz); IR (Nujol):  $\tilde{\nu}$  1190, 1175, 1097, 1059 cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>31</sub>H<sub>26</sub>AuF<sub>9</sub>IP: C 40.28, H 2.84; found: C 40.06, H 2.99.

**SP-4-4- and SP-4-3-[Au(*n*-C<sub>6</sub>F<sub>13</sub>)(Mes)](PPh<sub>3</sub>) (10) and (11).** It was prepared in the same way as for **9** from *n*-C<sub>6</sub>F<sub>13</sub>I (124  $\mu$ L, 0.556 mmol) and [Au(Mes)(PPh<sub>3</sub>)] (107 mg, 0.185 mmol). The obtained pale yellow solid was a mixture of **10** (81%) and its isomer **11** (19%). Yield: 126 mg (0.120 mmol), 65%. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane at 5 °C gave pale yellow crystals of pure **10**. Yield: 73 mg, 39%. M.p. 170–175 °C (dec); <sup>1</sup>H NMR (600.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =7.51–7.35 (m, 15H, Ph), 6.36 (s, 2H, H<sub>3</sub>, Mes), 2.13 (s, 6H, Me), 2.09 (s, 3H, Me); <sup>13</sup>C NMR (150.9 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =150.3 (m, C1, Mes), 136.68 (s, Mes), 136.64 (s, Mes), 135.3 (d,  $J_{P,C}$  = 7.8 Hz, C3, Ph), 132.2 (s, Ph), 129.8 (s, C3, Mes), 128.7 (d,  $J_{P,C}$  = 11.2 Hz, C2, Ph), 127.2 (d,  $J_{P,C}$  = 57.5 Hz, C1, Ph), 120.6–107.1 (several m, C-F) 23.7 (s, Me), 20.2 (s, Me); <sup>19</sup>F NMR (188.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =-79.5 (dtm, <sup>3</sup> $J_{P,F}$  = 39.7 Hz,  $J_{F,F}$  = 16.3 Hz, 2F, AuCF<sub>2</sub>), -81.1 (t,  $J_{F,F}$  = 10.1 Hz, 3F, CF<sub>3</sub>), -111.3 (m, 2F), -122.0 (m, 2F), -122.8 (m, 2F), -126.3 (m, 2F); <sup>31</sup>P NMR (81.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ =23.9 (t, <sup>3</sup> $J_{P,F}$  = 39.5 Hz); IR (Nujol):  $\tilde{\nu}$  1235, 1195 cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>33</sub>H<sub>26</sub>AuF<sub>13</sub>IP: C 38.69, H 2.56; found: C 38.61, H 2.58. NMR data of **11**: <sup>1</sup>H NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta$ =7.68–7.46 (m, 15H, Ph), 6.74 (d, 2H,

$^5J_{P,H} = 4.1$  Hz, H3, Mes), 2.44 (s, 3H, Me), 2.25 (s, 6H, Me);  $^{19}F$  NMR (188.3 MHz,  $CD_2Cl_2$ ):  $\delta = -81.1$  (m, 2F,  $AuCF_2$ ),  $-81.2$  (m, 3F,  $CF_3$ ),  $-113.8$  (m, 2F),  $-122.5$  (m, 2F),  $-123.1$  (m, 2F),  $-126.6$  (m, 2F);  $^{31}P$  NMR (81.0 MHz,  $CD_2Cl_2$ ):  $\delta = 28.3$  (tt,  $^3J_{P,F} = 29.7$  Hz,  $^4J_{P,F} = 5.3$  Hz).

**SP-4-4-[Au(*i*-C<sub>3</sub>F<sub>7</sub>)(Mes)I(PPh<sub>3</sub>)] (12).** To a solution of [Au(Mes)(PPh<sub>3</sub>)] (79 mg, 0.14 mmol) in  $CH_2Cl_2$  (6 mL) *i*-C<sub>3</sub>F<sub>7</sub>I (60  $\mu$ L, 0.41 mmol) was added. The mixture was irradiated at 402 nm for 15 s with stirring to give a yellow solution, which was concentrated to ca. 0.5 mL under vacuum, layered with *n*-hexane (10 mL) and allowed to stand in the dark until yellow crystals grew (2 days). The crystals were separated from the mother liquor and dried under vacuum. Yield: 12 mg (0.014 mmol), 9.8%;  $^1H$  NMR (300.1 MHz,  $CD_2Cl_2$ ):  $\delta = 7.53$ – $7.35$  (m, 15H, Ph), 6.32 (s, 2H, H<sub>3</sub>, Mes), 2.13 (s, 6H, Me), 2.06 (s, 3H, Me);  $^{19}F$  NMR (282.4 MHz,  $CD_2Cl_2$ ):  $\delta = -65.6$  (t,  $^3J_{P,F} = ^3J_{F,F} = 7.8$  Hz, 3F,  $CF_3$ ),  $-173.1$  (m, 1F, CF);  $^{31}P$  NMR (81.0 MHz,  $CD_2Cl_2$ ):  $\delta = 26.5$  (d of septets,  $^3J_{P,F} = 22.4$  Hz,  $^4J_{P,F} = 7.1$  Hz); The available amount of sample was too small to obtain a useful  $^{13}C$  NMR spectrum; elemental analysis calcd (%) for C<sub>30</sub>H<sub>26</sub>AuF<sub>7</sub>IP: C 41.21, H 3.00; found: C 41.33, H 3.12.

**trans-[AuBr<sub>2</sub>(*n*-C<sub>4</sub>F<sub>9</sub>)(PPh<sub>3</sub>)] (13).** *n*-C<sub>4</sub>F<sub>9</sub>I (137  $\mu$ L, 0.796 mmol) was added to a solution of [Au(Me)(PPh<sub>3</sub>)] (342 mg, 0.721 mmol) in  $CH_2Cl_2$  (20 mL). The mixture was irradiated with a 402 nm LED for 5 min and evaporated to dryness under vacuum. The resulting white solid containing complex **1** was redissolved in  $CH_2Cl_2$  (20 mL) and the solution was cooled at  $-70$  °C and protected from light. Then, a solution of Br<sub>2</sub> in  $CH_2Cl_2$  (2.8 mL, 0.26 M, 0.73 mmol of Br<sub>2</sub>) was added with stirring. The reaction mixture was slowly warmed to room temperature over 40 min then it was evaporated to dryness under vacuum. The orange residue was extracted with warm *n*-hexane (50 mL) to give a yellow extract. The residue was extracted with more warm *n*-hexane until the extract was almost colourless (2  $\times$  20 mL). The extracts were filtered through a cotton plug while protecting from light and evaporated to dryness. The residue was stirred with cold *n*-pentane (0° C, 3 mL) to give a yellow solid, which was filtered, washed with cold *n*-pentane (3 mL) and air dried. Yield: 452 mg (0.539 mmol), 75%. M.p. 98–100 °C (dec);  $^1H$  NMR (600.1 MHz,  $CD_2Cl_2$ ):  $\delta = 7.65$ – $7.51$  (m, 15H, Ph);  $^{13}C$  NMR (100.8 MHz,  $CD_2Cl_2$ ):  $\delta = 135.4$  (d,  $J_{P,C} = 9.6$  Hz, Ph), 132.9 (d,  $J_{P,C} = 2.6$  Hz, Ph), 129.2 (d,  $J_{P,C} = 11.7$  Hz, Ph), 126.5 (d,  $^1J_{P,C} = 58.1$  Hz, C-P), 119.5–109.2 (several m, *n*-C<sub>4</sub>F<sub>9</sub>);  $^{19}F$  NMR (188.3 MHz,  $CDCl_3$ ):  $\delta = -72.6$  (dt,  $J_{P,F} = 54.3$  Hz,  $J_{F,F} = 13.4$  Hz, 2F,  $AuCF_2$ ),  $-80.8$  (tt,  $J_{F,F} = 10.0$  and 2.2 Hz, 3F,  $CF_3$ ),  $-112.5$  (m, 2F),  $-125.8$  (m, 2F);  $^{31}P$  NMR (81.0 MHz,  $CDCl_3$ ):  $\delta = 27.4$  (t,  $^3J_{P,F} = 54.2$  Hz); IR (Nujol):  $\tilde{\nu}$  1237, 1197, 1093, 1075  $cm^{-1}$  (CF); elemental analysis calcd (%) for C<sub>22</sub>H<sub>15</sub>Br<sub>2</sub>F<sub>9</sub>PAu: C 31.53, H 1.80; found: C 31.57, H 1.82.

**trans-[Au(*n*-C<sub>4</sub>F<sub>9</sub>)Cl<sub>2</sub>(IPr)] (14).** A solution of PhICl<sub>2</sub> (36 mg, 0.13 mmol) in  $CH_2Cl_2$  (2.5 mL) was added to a light-protected solution of **2** (105 mg, 0.131 mmol) in  $CH_2Cl_2$  (5 mL) at  $-70$  °C with stirring. The mixture was allowed to warm at room temperature and then stirred for 45 min. The volatiles were removed under vacuum and the residue was stirred with *n*-pentane (5 mL) to give a yellow solid, which was isolated by filtration and air dried. Yield: 76 mg (0.87 mmol), 66%. M.p. 149–151 °C (dec);  $^1H$  NMR (600.1 MHz,  $CD_2Cl_2$ ):  $\delta = 7.57$  (t,  $J_{H,H} = 7.2$  Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.38 (d,  $J_{H,H} = 7.8$  Hz, 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.33 (s, 2H, CH=CH), 2.86 (sept,  $J_{H,H} = 6.6$  Hz, 4H, *CHMe*<sub>2</sub>), 1.38 (d,  $J_{H,H} = 6.6$  Hz, 12H, Me), 1.13 (d,  $J_{H,H} = 7.2$  Hz, 12H, Me);  $^{13}C$  NMR (150.9 MHz,  $CD_2Cl_2$ ):  $\delta = 166.3$  (t,  $^3J_{C,F} = 16.6$  Hz, N<sub>2</sub>CAu), 146.6 (Ar), 133.3 (Ar), 131.6 (Ar), 126.3 (CH=CH), 124.8 (Ar), 123.3–109.3 (several m, C-F), 29.3 (*CHMe*<sub>2</sub>), 26.6 (Me), 22.7 (Me);  $^{19}F$  NMR (188.3 MHz,  $CD_2Cl_2$ ):  $\delta = -81.9$  (tt,  $J_{F,F} = 9.8$  and 2.6 Hz, 3F,  $CF_3$ ),  $-91.6$  (t,  $J_{F,F} = 16.7$  Hz, 2F,  $AuCF_2$ ),  $-117.0$  (m, 2F),  $-126.6$  (m, 2F); IR (Nujol):  $\tilde{\nu}$  1228, 1194, 1131, 1086  $cm^{-1}$  (CF); elemental analysis calcd (%) for C<sub>31</sub>H<sub>36</sub>Cl<sub>2</sub>F<sub>9</sub>AuN<sub>2</sub>: C 42.53, H 4.14, N 3.20; found: C 42.56, H 4.20, N 3.04.

**trans-[Au(*n*-C<sub>4</sub>F<sub>9</sub>)Br<sub>2</sub>(IPr)] (15).** It was prepared in the same way as for **14** from Br<sub>2</sub> (0.13 mmol) and **2** (102 mg, 0.127 mmol). Orange solid. Yield: 75 mg (0.078 mmol), 61%. M.p. 157–161 °C (d);  $^1H$  NMR (200.1 MHz,  $CD_2Cl_2$ ):  $\delta = 7.56$  (t,  $^3J_{H,H} = 7.2$  Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.37 (d,  $^3J_{H,H} = 7.7$  Hz, 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.35 (s, 2H, CH=CH), 2.99 (sept,  $^3J_{H,H} = 6.8$  Hz, 4H, *CHMe*<sub>2</sub>), 1.38 (d,  $^3J_{H,H} = 6.6$  Hz, 12H, Me), 1.12 (d,  $^3J_{H,H} = 6.8$  Hz, 12H, Me);  $^{13}C$  NMR (150.9 MHz,  $CD_2Cl_2$ ):  $\delta = 163.5$  (t,  $^3J_{C,F} = 16.6$  Hz, N<sub>2</sub>CAu), 146.5 (Ar), 133.7 (Ar), 131.6 (Ar), 126.6 (CH=CH), 124.8 (Ar), 122.9–109.2 (several m, C-F), 29.4 (*CHMe*<sub>2</sub>), 26.7 (Me), 23.0 (Me);  $^{19}F$  NMR (188.3 MHz,  $CD_2Cl_2$ ):  $\delta = -81.9$  (tt,  $J_{F,F} = 9.8$  and 2.7 Hz, 3F,  $CF_3$ ),  $-83.3$  (t,  $J_{F,F} = 13.6$  Hz, 2F,  $AuCF_2$ ),  $-114.7$  (m, 2F),  $-126.6$  (m, 2F); IR (Nujol):  $\tilde{\nu}$  1232, 1197, 1129  $cm^{-1}$  (CF); elemental analysis calcd (%) for C<sub>31</sub>H<sub>36</sub>Br<sub>2</sub>F<sub>9</sub>AuN<sub>2</sub>: C 38.61, H 3.76, N 2.90; found: C 38.35, H 3.76, N 2.86.

**trans-[Au(*i*-C<sub>3</sub>F<sub>7</sub>)Cl<sub>2</sub>(IPr)] (16).** It was prepared in the same way as for **14**, from PhICl<sub>2</sub> (61 mg, 0.22 mmol) and **5** (110 mg, 0.183 mmol). The mixture was stirred for 12 h at room temperature and worked-up in the same way to give a yellow solid. Yield: 124 mg (0.150 mmol), 82%. M.p. 187–190 °C (dec);  $^1H$  NMR (200.1 MHz,  $CD_2Cl_2$ ):  $\delta = 7.57$  (t,  $^3J_{H,H} = 7.8$  Hz, 2H, *p*-C<sub>6</sub>H<sub>3</sub>), 7.37 (d,  $^3J_{H,H} = 7.4$  Hz, 4H, *m*-C<sub>6</sub>H<sub>3</sub>), 7.36 (s, 2H, CH=CH), 2.86 (sept,  $^3J_{H,H} = 6.8$  Hz, 4H, *CHMe*<sub>2</sub>), 1.36 (d,  $^3J_{H,H} = 6.7$  Hz, 12H, Me), 1.12 (d,  $^3J_{H,H} = 6.8$  Hz, 12H, Me);  $^{13}C$  NMR (150.9 MHz,  $CD_2Cl_2$ ):  $\delta = 163.0$  (m, N<sub>2</sub>CAu), 146.6 (s, Ar), 133.1 (s, Ar), 131.7 (s, Ar), 126.4 (s, CH=CH), 124.7 (s, Ar), 122.6 (qdq,  $^1J_{F,C} = 310.8$  Hz,  $^2J_{F,C} = 26.4$  Hz,  $^3J_{F,C} = 4.5$  Hz,  $CF_3$ ), 96.2 (d of septets,  $^1J_{F,C} = 233.6$  Hz,  $^2J_{F,C} = 35.9$  Hz, CF), 29.3 (*CHMe*<sub>2</sub>), 26.7 (Me), 22.5 (Me);  $^{19}F$  NMR (188.3 MHz,  $CD_2Cl_2$ ):  $\delta = -68.5$  (d,  $^3J_{F,F} = 8.5$  Hz, 6F,  $CF_3$ ),  $-177.9$  (sept,  $^3J_{F,F} = 8.5$  Hz, 1F, CF); IR (Nujol):  $\tilde{\nu}$  1292, 1275, 1210, 1191  $cm^{-1}$  (CF); elemental analysis calcd (%) for C<sub>30</sub>H<sub>36</sub>Cl<sub>2</sub>F<sub>7</sub>AuN<sub>2</sub>: C 43.65, H 4.40, N 3.39; found: C 43.50, H 4.38, N 3.29.

**trans-[Au(*n*-C<sub>4</sub>F<sub>9</sub>)Me<sub>2</sub>(PPh<sub>3</sub>)] (18).** MgMeBr (2.8 M solution in Et<sub>2</sub>O, 1.05 mmol) was added to a solution of **13** (293 mg, 0.350 mmol) in THF (20 mL) at  $-70$  °C protected from light. The mixture was allowed to warm at room temperature and stirred for 30 min in the dark. Then, H<sub>2</sub>O (0.1 mL) was added and the mixture was stirred for 15 min and evaporated to dryness under vacuum. The residue was stirred with  $CH_2Cl_2$  (20 mL) and excess of MgSO<sub>4</sub> for 40 min. The suspension was filtered over celite. The solid material was extracted with more  $CH_2Cl_2$  (30 mL) and the combined  $CH_2Cl_2$  solutions were evaporated to dryness. The resulting residue was extracted with *n*-pentane (3  $\times$  3 mL). The extract was filtered and concentrated under vacuum to give a white solid. Yield: 128 mg (0.181 mmol), 52%. M.p. 128–130 °C (dec);  $^1H$  NMR (600.1 MHz,  $CD_2Cl_2$ ):  $\delta = 7.58$ – $7.50$  (m, 15H, Ph), 0.11 (d,  $^3J_{P,H} = 5.3$  Hz, 6H, Me);  $^{13}C$  NMR (150.9 MHz,  $CD_2Cl_2$ ):  $\delta = 134.7$  (d,  $J_{P,C} = 10.8$  Hz, C<sub>3</sub>, Ph), 132.2 (s, Ph), 129.3 (d,  $J_{P,C} = 11.2$  Hz, C<sub>2</sub>, Ph), 126.9 (d,  $J_{P,C} = 57.3$  Hz, C<sub>1</sub>, Ph), 121.2–108.4 (several m, C-F), 13.7 (m, Me);  $^{19}F$  NMR (188.3 MHz,  $CD_2Cl_2$ ):  $\delta = -81.3$  (tt,  $J_{F,F} = 10.1$  and 3.2 Hz, 3F,  $CF_3$ ),  $-96.9$  (dt,  $J_{P,F} = 38.6$  Hz and  $J_{F,F} = 13.9$  Hz, 2F,  $AuCF_2$ ),  $-116.9$  (m, 2F),  $-126.0$  (m, 2F);  $^{31}P$  NMR (81.0 MHz,  $CD_2Cl_2$ ):  $\delta = 30.0$  (t,  $^3J_{P,F} = 38.4$  Hz); IR (Nujol):  $\tilde{\nu}$  1346, 1233, 1190, 1100, 1073  $cm^{-1}$  (CF); elemental analysis calcd (%) for C<sub>24</sub>H<sub>21</sub>F<sub>9</sub>PAu: C 40.69, H 2.99; found: C 40.93, H 2.74.

**SP-4-4-[Au(*n*-C<sub>4</sub>F<sub>9</sub>)(Me)I(PPh<sub>3</sub>)] (19).** A solution of **18** (84 mg, 0.119 mmol) in  $CH_2Cl_2$  (20 mL) was sequentially treated with HOTf (140  $\mu$ L of a 0.85 M solution in Et<sub>2</sub>O, 0.119 mmol) and NBU<sub>4</sub>I (45 mg, 0.12 mmol) at room temperature in the dark. The mixture was stirred for 2 min and evaporated to dryness under vacuum. The residue was stirred with 4:1 *n*-pentane:Et<sub>2</sub>O (30 mL) in the dark. The suspension was filtered with a cannula equipped with a cotton filter, and the filtrate was transferred to a light-protected flask and evaporated to dryness. The resulting residue was stirred with *n*-pentane (3 mL). The suspension was filtered and the white solid was washed with *n*-pentane (3  $\times$  2 mL) and air dried. Yield: 20

mg (0.025 mmol), 20%. M.p. 89–92 °C (dec); <sup>1</sup>H NMR (300.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=7.65–7.51 (m, 15H, Ph), 1.41 (d, <sup>3</sup>J<sub>P,H</sub> = 5.6 Hz, 3H, Me); <sup>19</sup>F NMR (282.4 MHz, CDCl<sub>3</sub>): δ=-80.8 (tt, J<sub>F,F</sub> = 9.7 and 2.4 Hz, 3F, CF<sub>3</sub>), -83.5 (dt, J<sub>P,F</sub> = 40.7 Hz and J<sub>F,F</sub> = 13.1 Hz, 2F, AuCF<sub>2</sub>), -113.3 (m, 2F), -125.8 (m, 2F); <sup>31</sup>P NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ=27.0 (t, <sup>3</sup>J<sub>P,F</sub> = 40.5 Hz); an useful <sup>13</sup>C NMR spectrum was not obtained because complex **19** partially decomposed during the measurement; IR (Nujol):  $\tilde{\nu}$  1346, 1223, 1127, 1097, 1073 cm<sup>-1</sup> (CF); elemental analysis calcd (%) for C<sub>23</sub>H<sub>18</sub>IF<sub>9</sub>PAu: C 33.68, H 2.21; found: C 33.70, H 2.04.

**Crystal Structure Determinations.** Single crystals of **1** and **2** were obtained by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane solution. Single crystals of **9**, **10**, **12** and **13** were obtained by liquid diffusion between a CH<sub>2</sub>Cl<sub>2</sub> solution and *n*-hexane. The compounds were measured on a Bruker D8 SMART diffractometer at 100K. Data were collected using a high brilliance microfocus sealed tube with Mo-K $\alpha$  radiation (0.71073 Å) in omega and phi-scans. The structures were solved by dual methods. All were refined anisotropically on F<sup>2</sup>. The methyl groups were refined using rigid groups and the other hydrogens were refined using a riding mode. *Special features of refinement:* (a) In **1** there was a poorly-resolved region of residual electron density that was interpreted as a disorder over two positions of the AuCF<sub>2</sub> carbon atom (97%) and an iodine atom (3%). Different sets of data were measured all of them showing the same problem. (b) In **2** the perfluorobutyl ligand was disordered over two positions with a ca. 51:49 occupancy distribution. (c) In **13** the perfluorobutyl ligand of one of the two independent molecules was disordered over two positions with a ca. 88:12 occupancy distribution. In this case the atoms of the minor positions were refined as isotropic. Crystal data and details about data acquisition and structure refinement are included in the Supporting Information. CCDC 1913442 (**1**), 1913443 (**13**), 1913444 (**2**), 1913445 (**12**), 1913446 (**9**), 1913447 (**10**), contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.

## Acknowledgements

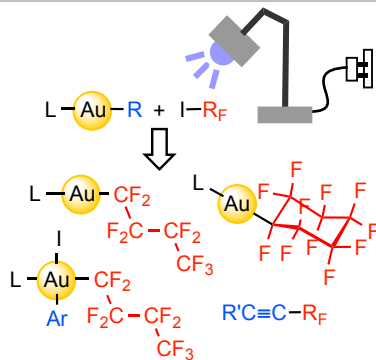
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Irradiation with a mild light source (402 nm LED) can activate reactions between iodoperfluoroalkanes and Au(I) organometallic complexes. These reactions proceed through a radical mechanism and have afforded the first isolated of Au(I) or Au(III) complexes containing perfluoroalkyl chains, including rare perfluorocyclohexyl metal complexes.



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**Photoinitiated Reactions of Haloperfluorocarbons with Gold(I) Organometallic Complexes. Perfluoroalkyl Gold(I) and Gold(III) Complexes**