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Synthesis of Au(I) Trifluoromethyl Complexes. Oxidation to Au(III) and Reductive Elimination of Halotrifluoromethanes

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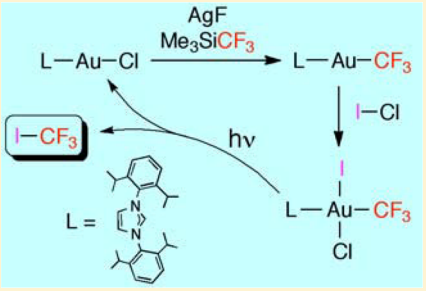
Supporting Information

ABSTRACT: Au(I) trifluoromethyl complexes [Au(CF_3)L] (L = *N*-heterocyclic carbene (NHC), isonitrile, phosphine, P(OMe)$_3$) and [Au$_2$(CF_3)$_2$(μ-dppe)] are prepared by reaction of [Au(X)L] (X = Cl, I) or [Au$_2$Cl$_2$(μ-dppe)], respectively, with AgF and Me_3SiCF_3. The analogous reaction of PPN[Au(C_6F_5)Cl] (PPN$^+$ = [Ph_3PNPPh_3]$^+$) gives a mixture of complexes of the type PPN[Au(CF_3)$_x$(C_6F_5)$_{2-x}$] (x = 0, 1, 2). Single crystals of the new complex PPN[Au(CF_3)(C_6F_5)] are obtained by liquid diffusion from this mixture, and its crystal structure was determined by X-ray diffraction. Acyclic diaminocarbene complexes [Au(CF_3){C(NEt_2)(NHR)}] (R = ^{t}Bu, 2,6-dimethylphenyl) are obtained by reaction of [Au(CF_3)(CNR)] with $NHEt_2$. Oxidation of the NHC complex [Au(CF_3)(IPr)] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) with $PhICl_2$, Br_2, I_2 or ICl affords [Au(CF_3)(X)(Y)(IPr)] (X = Y = Cl, Br I; X = Cl, Y = I). The dicloro, dibromo, and chloro(iodo) complexes are stable in solution in the dark. In contrast, the diiodo complex is unstable and decomposes to [AuI(IPr)] and ICF_3. Under photoirradiation, complexes [Au(CF_3)(X)(Y)(IPr)] undergo reductive elimination to give YCF_3 and [AuX(IPr)] (X = Y = Cl, Br; X = Cl, Y = I).



INTRODUCTION

Following the demand for high added-value trifluoromethylated aromatic compounds,[1−4] new synthetic protocols for the selective trifluoromethylation of aromatic substrates involving in situ generated or preformed trifluoromethyl complexes of Pd, Cu, or Ag have been recently developed.[2,5−13] These important advances have shown the potential of fluorinated organometallic compounds in organic synthesis and stimulated the research on new types of transition-metal perfluoroalkyls.

Reductive elimination of trifluoromethylated compounds is a key step in many of these reactions, but due to the stability of the metal−CF_3 bond,[14−16] it is generally a slow process.[17−20] Thus, Toste and co-workers have very recently shown that thermal decomposition of complexes of the type [Au(Ar)(CF_3)I(PR_3)], prepared by oxidative addition of CF_3I to [Au(Ar)(PR_3)], affords ArI instead of $ArCF_3$.[21] This contrasts with the very mild elimination of biaryls and nonfluorinated alkylarenes from the corresponding diorganogold(III) complexes.[22−26] However, the above-mentioned work of the Toste group also reports that fast $ArCF_3$ reductive elimination at room or low temperature occurs by abstraction of the iodo ligand from the studied Au(III) complexes. This suggests the viability of gold-catalyzed arylic trifluoromethylation. Apart from this report, reductive elimination of trifluoromethylated compounds from Au(III) trifluoromethyl complexes has never been documented, and very little is known about the reactivity and potential applications in organic synthesis of gold perfluoroalkyl derivatives.[21,27,28]

To explore the reactivity and potential synthetic applications of Au(I) and (III) trifluoromethyl complexes, we initiated a study from a different point of view that involves, in the first stage, the synthesis of Au(I)CF_3 complexes, followed by investigating oxidative addition reactions with halogens and pseudohalogens. A second step will be the study of transmetalation reactions with the resulting Au(III)CF_3 complexes.

The synthesis of gold(I) perfluoroalkyls is still a challenging objective.[14−16,28] Thus, the first Au(I) trifluoromethyl was obtained in the reaction of [AuMe(PPh_3)] with ICF_3 to give [Au(CF_3)(PPh_3)].[29] Complexes of the type [Au(CF_3)L] (L = PMe_3, PEt_3, PPh_3, PCy_3, PMe_2Ph, PF_2R, CNMe) were prepared by using Cd(CF_3)$_2$ as transmetalating agent,[30−33] or by the reaction of [Au(OR)L] (R = CH(CF_3)$_2$, Ph) with Me_3SiCF_3.[34] Recently, salts of the [Au(CF_3)$_2$]$^-$ anion have been obtained by reaction of AuCl or [AuCl(tht)] with Me_3SiCF_3 and F^-.[35,36] Interestingly, BF_3-assisted hydrolysis of [Au(CF_3)$_2$]$^-$ gives [Au(CF_3)(CO)],[37] which undergoes CO substitution by tht, ^{t}BuNC, MeCN, or py ligands,[36] making this carbonyl complex a valuable synthon to prepare species containing the Au(CF_3) unit. However, the synthesis of these complexes requires previous preparation of [PPh_4][Au(CF_3)$_2$] and the handling of moisture-sensitive and unstable compounds.

Most Au(III) trifluoromethyl complexes have been obtained by oxidative addition to Au(I) complexes. Thus, addition of

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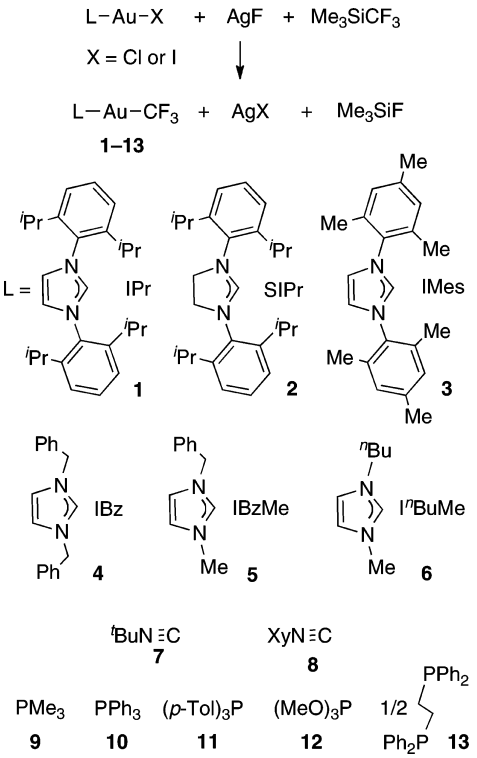
halogens to $[Au(CF_3)(PR_3)]$ or $[Au(CF_3)_2]^-$ gave $[Au(CF_3)X_2(PR_3)]$ (X = Br, I; R = Me, Et, Ph)[30,31] or $[Au(CF_3)_2X_2]^-$ (X = Cl, Br, I),[36] respectively. Oxidative addition of ICF_3 to $[Au(CF_3)(PR_3)]$ (R = Me, Et)[30,31] or $[AuMe(PMe_3)]$[29,38] gave $[Au(CF_3)_2I(PR_3)]$, or mixtures of $[AuMe_2(CF_3)(PMe_3)]$ and $[AuI(PMe_3)]$, respectively. Photoinitiated oxidative addition of ICF_3 to $[Au(Ar)(PR_3)]$ (R = Cy or Ph) gave $[Au(Ar)(CF_3)I(PR_3)]$.[21] $Au(CF_3)_3$ and $[Au(CF_3)_2(\mu\text{-}X)]_2$ were obtained by condensation of Au atoms with XCF_3 (X = Br or I).[39,40] Only one trifluoromethylation reaction of a Au(III) compound has been reported, namely, the reaction of $AuCl_3$ with Me_3SiCF_3 and F^-, which gave $[Au(CF_3)_4]^-$.[36] The reaction of $[Au(CN)_4]^-$ with ClF gave a mixture of complexes of the type $[AuF_xCl_y(CF_3)_{4-x-y}]^-$ (x = 0–4, y = 0–2).[41]

In the search for straighforward methods to prepare Au(I) trifluoromethyl compounds, we turned our attention to Ag(I) trifluoromethyl complexes. Solutions of "$Ag(CF_3)$" can be generated by reaction of AgF with Me_3SiCF_3 and have been used as transmetalating agents toward compounds of elements from the groups 14–16,[42] as well as in the trifluoromethylation of organic substrates.[12,13,43–46] Herein, we report the synthesis of a series of Au(I) trifluoromethyl complexes by reaction of easily available $[AuCl(L)]$ complexes with AgF and Me_3SiCF_3, which includes the first gold trifluoromethyl complexes containing carbene ligands. We have also studied the oxidative addition of $PhICl_2$, Br_2, I_2 and ICl to $[Au(CF_3)(IPr)]$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ydene). The isolated Au(III) complexes, except for the diiodo derivative, are thermally stable, but on photoirradiation undergo reductive elimination to give YCF_3 and $[AuX(IPr)]$ (X = Y = Cl, Br; X = Cl, Y = I).

RESULTS AND DISCUSSION

Synthesis of Au(I) Trifluoromethyl Complexes. Complexes $[AuXL]$ (X = Cl, L = IPr, ^{t}BuNC, XyNC, PMe_3, PPh_3, $P(p\text{-Tol})_3$, $P(OMe)_3$; X = I, L = SIPr, IMes, IBz, IBzMe, I^{n}BuMe) or $[Au_2Cl_2(\mu\text{-dppe})]$ react with AgF (1.5–1.8 equiv) and an excess of Me_3SiCF_3 at room temperature to give trifluoromethyl complexes **1**–**13** (Scheme 1). The Au(I) trifluoromethyl complexes were separated from the reaction crude by column chromatography on silica and isolated in yields ranging from 25 to 78%. Compounds **7**,[36] **9**,[29,30,34] and **10**[30,34] have been previously reported (see the Introduction), but the present method allows one to prepare them directly from the corresponding chloro complexes, without using the toxic $Cd(CF_3)_2$. The new trifluoromethyl complexes are air-stable and can be stored at room temperature, except in the case of the trimethylphosphite complex **12**, which slowly decomposes to metallic gold at room temperature. The low yields obtained in some cases are attributed to the formation of side products, or to partial decomposition during chromatographic separation. Thus, NMR analysis of the reaction crudes revealed that, although complexes **1**–**13** are the major reaction products, significant amounts of the known complexes $[AuL_2]^+$ were also formed. The highest amount of the cationic side product was observed for L = IMes, which gave a ca. 1:1 mixture of **3** and $[Au(IMes)_2]^+$.[47] Minor amounts of $[AuL_2]^+$ were detected for L = IBz,[48] IBzMe,[48] I^{n}BuMe,[49] XyNC, and PMe_3. In the two latter cases, the ^{19}F NMR and ESI-MS spectra of the crude revealed the presence of $[Au(CF_3)_2]^-$ (see the Experimental Section). On the basis of this observation, we hypothesized that salts of the type $[AuL_2][Au(CF_3)_2]$ could be formed by ligand exchange between two molecules of

Scheme 1. Synthesis of Gold(I) Trifluoromethyl Complexes (1–13)

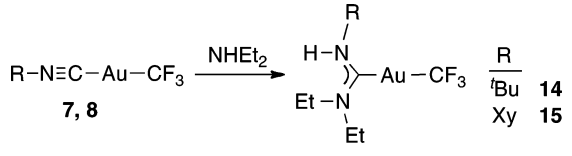


$[Au(CF_3)L]$. However, the NMR and ESI-MS spectra of the isolated neutral complexes do not show any evidence of ligand exchange at room temperature (see below), suggesting that these byproducts should be formed by side reactions or by ligand exchange catalyzed by Ag(I) salts present in the reaction mixture.

The reaction of $PPN[Au(C_6F_5)Cl]$ ($PPN^+ = [Ph_3PNPPh_3]^+$) with AgF and Me_3SiCF_3 gave a mixture containing mainly complexes $PPN[Au(CF_3)_x(C_6F_5)_{2-x}]$ (x = 0, 1, 2) and minor amounts of $[Ag(CF_3)_2]^-$, which were detected in the reaction crude by negative ESI-MS. Complexes $[Au(CF_3)_2]^-$, $[Au(C_6F_5)_2]^-$, and $[Ag(CF_3)_2]^-$ were also identified by ^{19}F NMR spectroscopy (see the Experimental Section). Single crystals of the new complex $PPN[Au(CF_3)(C_6F_5)]$ were obtained by liquid diffusion from this mixture, and its crystal structure was determined by X-ray diffraction (see the Crystal Structures section). To the best of our knowledge, this is the first complex containing both CF_3 and C_6F_5 ligands bonded to the same metal.

Au(I) trifluoromethyl complexes containing ADC (acyclic diaminocarbene) ligands (**14** and **15**, Scheme 2) were obtained by reaction of the isocyanide complexes **7** or **8** with $NHEt_2$. They are less stable than their NHC counterparts and must be stored at low temperature.

Scheme 2. Synthesis of Gold(I) Trifluoromethyl Complexes 14 and 15 Containing ADC Ligands



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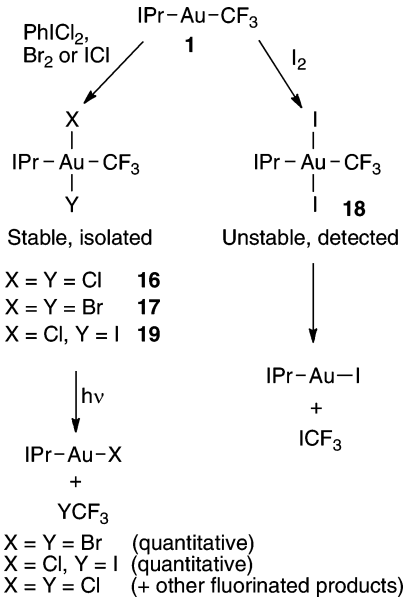
Reactions of Complex 1 with $PhICl_2$, Br_2, or I_2. The reactions of **1** with 1 equiv of $PhICl_2$ or an excess of Br_2 (1.2−3 equiv) led to *trans*-[$Au(CF_3)X_2(IPr)$] (X = Cl (**16**), Br (**17**)), which were isolated as white or yellow solids, respectively (Scheme 3). Their *trans* configuration was determined by single-crystal X-ray diffraction (see the Crystal Structures section).

Scheme 3. Formation and Decomposition of Au(III) Trifluoromethyl Complexes



Remarkably, good yields of **16** were obtained only if the addition of $PhICl_2$ is carried out at low temperature (−90 °C). Carrying out the addition at room temperature led to mixtures containing mainly **16**, [$AuCl_3(IPr)$],[50] [AuCl(IPr)],[51] $ClCF_3$, and **1** (see the Supporting Information). The side products [AuCl(IPr)] and $ClCF_3$ are not formed by reductive elimination from **16** because it is stable in solution (see below). Instead, they could be formed through reductive elimination from a Au(III) intermediate, as previously reported for the reaction of [Au(Me)(IPr)] with I_2,[52] or by direct halogenation of the Au−CF_3 bond. [$AuCl_3(IPr)$] could be formed through oxidation of [AuCl(IPr)] by the remaining $PhICl_2$.

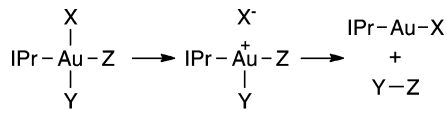
Both **16** and **17** are thermally stable in the solid state (decomposition temperature > 200 °C), as well as in solution under ambient laboratory light. Thus, they remained unaltered after heating their CD_2Cl_2 solutions at 80 °C, for 16 h. In contrast, **17** was quantitatively converted into [AuBr(IPr)] and $BrCF_3$ on irradiation of a CD_2Cl_2 solution with UV−visible light of λ > 260 nm, whereas irradiation of **16** under the same conditions gave a solution containing [AuCl(IPr)] (main organometallic product), $ClCF_3$, and several organic fluorinated products that could not be identified (see the Supporting Information).

The reaction of **1** with I_2 (1 or 3 equiv) at room temperature quantitatively gave [AuI(IPr)][51] and ICF_3 (Scheme 3). In order to detect possible reaction intermediates, we mixed the reagents in an NMR tube at −90 °C, inserted the tube into the NMR probe at −80 °C, and progressively increased the temperature (see the Supporting Information). At low temperatures (from −80 to −40 °C), **1** was the main component of the reaction mixture, and [AuI(IPr)], ICF_3, and a new complex (**18**) were also detected. A temperature rise led to progressive reduction of the amount of **1**, with a concomitant increase of **18**, [AuI(IPr)] and ICF_3. Finally, at room temperature, the signals of **1** and **18** progresively vanished, and only those of [AuI(IPr)] and ICF_3 were finally observed. Considering the behavior of **18** and the similarity of its ^1H NMR resonances with those of **16** or **17**, we assigned it to the oxidative addition product *trans*-[$Au(CF_3)I_2(IPr)$]. The simultaneous presence of **1**, **18**, [AuI(IPr)], and ICF_3 in the reaction mixture suggests that the rates of I_2 oxidative addition to **1** and ICF_3 reductive elimination from **18** do not differ greatly.

The reaction of **1** with ICl (1 equiv) gave quantitatively (*SP*-4-2)-[$Au(CF_3)(Cl)(I)(IPr)$] (**19**, Scheme 3), which was isolated as a yellow-orange crystalline solid by crystallization at low temperature. Its NMR spectra (see below) suggest that, in **19**, the CF_3 and IPr ligands are disposed in a *trans* arrangement, as for **16**−**18**. In addition, we carried out several attempts to determine its X-ray structure. Although a full structure determination was not possible because of the low quality of the crystals measured, the obtained data confirmed the *trans* disposition of the CF_3 and IPr ligands. It is noteworthy that, although a large number of halogen oxidative additions to Au(I) complexes have been reported, **19** is the first isolated Au(III) complex resulting from an interhalogen oxidative addition reaction. Complex **19** is stable in the solid state at room temperature, but in solution (CD_2Cl_2), at room temperature, and in the dark, it undergoes a slow partial halogen redistribution to give the dichloro and diiodo complexes **16** and **18**. Thus, after 4 days, the amounts of **16**, **18**, and **19** were in a 1:1:14 relative proportion. This contrasts with the fast halogen scrambling reported in complexes [$AuCl_xBr_{3-x}L$] (L = tertiary phosphine or phosphole).[53,54] Along with these compounds, small amounts of [AuI(IPr)] and ICF_3 are also observed, likely formed through reductive elimination from **18**. Analogously to **17**, complex **19** underwent reductive elimination after 30 min under photoirradiation to quantitatively give [AuCl(IPr)] and ICF_3.

Previous studies on the reductive elimination of R-I, Ar-Cl, or R-F from complexes *trans*-[$Au(R)I_2(IPr)$] (R = alkyl),[52,55] *trans*-[$Au(Ar)Cl_2(IPr)$] (Ar = C_6H_5, C_6F_5),[56] or *cis*-[$Au(R)F_2(IPr)$],[55] respectively, suggest that these reactions proceed through halide dissociation, to give a cationic tricoordinated intermediate, which decomposes to give the organic halide and the Au(I) complex (Scheme 4). According to this mechanism,

Scheme 4. Proposed Mechanism for the Reductive Elimination from Au(III) Complexes



X	Y	Z	ref.
I	I	Alkyl	52, 55
Cl	Cl	Aryl	56
F	Alkyl	F	55
Cl	Cl	CF_3	this work
Br	Br	CF_3	this work
I	I	CF_3	this work
Cl	I	CF_3	this work

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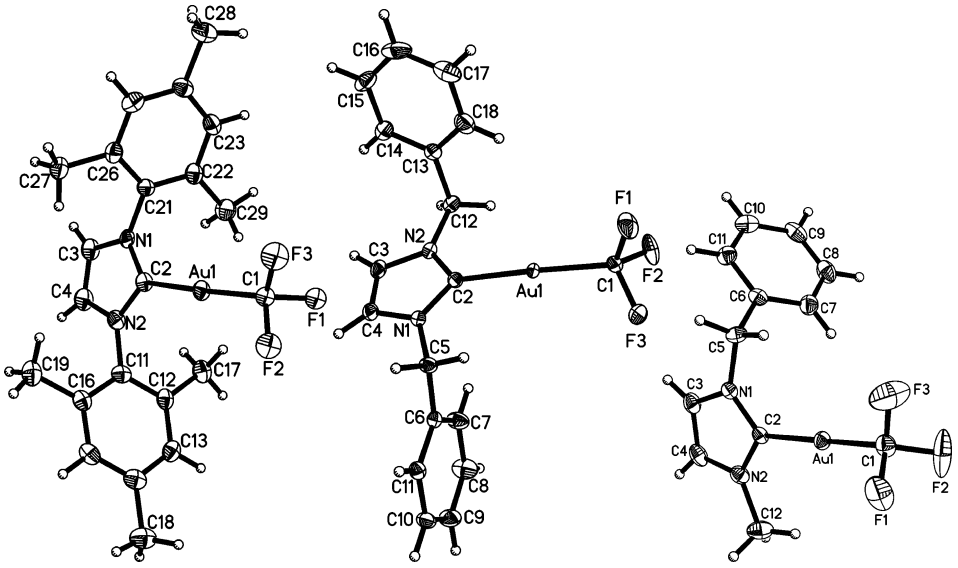

Figure 1. Molecular structures of complexes **3** (left), **4** (middle), and **5** (right). Thermal ellipsoids have been drawn at 50% probability.

the kinetic barrier to reductive elimination should be smaller as the Au−halide dissociation energy becomes lower.[57] Although Au(III) is considered as a soft acid in aqueous solution,[58] the computed dissociation energies of complexes $[AuX_4]^-$ in the gas phase follow the sequence $F^- > Cl^- > Br^- > I^-$,[59−61] which is in line with the generally observed lower stability of Au(III) iodo complexes with respect to their chloro or bromo analogues.[62] Thus, the easier reductive elimination observed in the diiodo complex **18** can be attributed to a lower halide dissociation energy. In addition, the kinetic stability of **16** with respect to *trans*-$[Au(Ph)Cl_2(IPr)]$[56] could be attributed to the strengthening of the Au−Cl bond produced by the enhanced Lewis acidity of the metal center in the trifluoromethyl complex.

Reductive elimination in complexes **16**, **17**, and **19** could take place by photoexcitation to a state where one of the Au−halogen bonds is weakened. Spectroscopic and theorethical studies on Au(III) carbene halides show that the lowest-energy excited states of these complexes are of the LMCT type, involving the transfer of electron density from the halide-based HOMO to the metal-based LUMO, which presents Au−X antibonding character.[48,56,63,64] Similarly, the lowest-energy absorption maxima of **16**−**18** move to lower energies as the halogen electronegativity decreases, which is characteristic for LMCT transitions (λ_{max} = 272, 312, and 365 nm for **16**, **17**, and **18**, respectively), and **19** gives two maxima at 291 and 376 nm, which are assigned to Cl → Au and I → Au LMCT transitions, respectively (the spectra are included in the Supporting Information). Interestingly, complex **19** reductively eliminates ICF_3 instead of $ClCF_3$. According to the proposed mechanism, this could be explained by considering that photoexcitation of the lower energy LMCT (I → Au) state would increase the electron density al the metal center and weaken the Au−Cl bond, leading to Cl^- dissociation, to give $[Au(CF_3)I(IPr)]^+$, which would reductively eliminate ICF_3.

To obtain experimental evidence of the proposed photoactivated halide dissociation, we treated a CD_2Cl_2 solution of the dibromo complex **17** with $(N^nBu_4)Cl$. However, halide exchange took place in the dark, giving a mixture of **16**, **17**, and $[Au(CF_3)(Br)(Cl)(IPr)]$,[65] probably through an associative pathway.[66] In another experiment, a CD_2Cl_2 solution containing **16** and **17** was stored in the dark for 1 h, and then it was irradiated for a short time to avoid complete decomposition. NMR analysis of the mixture showed that no changes occurred in the dark, but after irradiation, **16**, **17**, $[Au(CF_3)(Br)(Cl)(IPr)]$, and photodecomposition products were detected (see the Supporting Information). Formation of the mixed-halogen complex suggests that photoirradiation can induce halide dissociation on these complexes, although this complex could also be formed by halide exchange between **16** or **17** and the decomposition products [AuX(IPr)] (X = Cl, Br).[67]

Spectroscopic Characterization. The $\nu(C{\equiv}N)$ band of compound **8** appears at 2215 cm^{-1}, a value similar to those reported for the analogous chloro[68] or nitrato[69] complexes (2215.8 or 2215 cm^{-1}, respectively), which is in agreement with the high electronegativity of the CF_3 group.

The NMR data of compounds **7**, **9**, and **10** coincide with those previously reported.[30,31,36] The $\delta(^{19}F)$ values of the CF_3 groups of complexes $[Au(CF_3)L]$ (**1**−**15**) and PPN$[Au(CF_3)(C_6F_5)]$ fall in a narrow range (from −31.4 to −26.1 ppm), whereas, in complexes $[Au(CF_3)(X)(Y)(IPr)]$, they spread over a wider range depending on the nature of the halogens (I: −9.5 ppm; Br: −24.5 ppm; Cl: −32.4 ppm; Cl and I: −21.5 ppm). In the phosphine complexes **9**−**12**, the ^{19}F NMR signal appears as a doublet due to coupling with ^{31}P. Conversely, a quartet is observed in their $^{31}P\{^1H\}$ NMR spectra. The ^{19}F and $^{31}P\{^1H\}$ NMR spectra of complex **13** display a virtual doublet and a second-order multiplet, respectively, corresponding to an $AA'X_3X'_3$ spin system (see the Supporting Information).

In the $^{13}C\{^1H\}$ NMR spectra, the gold-bound carbons of the carbene and isonitrile ligands give a quartet due to their coupling with the fluorine nuclei of CF_3 groups. The $^3J_{FC}$ values are smaller for the Au(I) complexes (12.8−19.8 Hz) than for the Au(III) complexes (**16**: 28.5; **17**: 29.5; **19**: 27.9 Hz). The existence of these couplings suggests that ligand exchange, as found in some Cu(I) or Ag(I) trifluoromethyl complexes, which are in equilibrium with ionic species of the type $[ML_2][M(CF_3)_2]$,[10,13,70,71] does not occur (in CD_2Cl_2). The Au-bound carbenic carbon of the IPr ligand is shielded on going from the Au(I) complex **1** (188.5 ppm) to its Au(III) congeners **16**, **17**, and **19** (165.5, 168.0, and 162.5 ppm,

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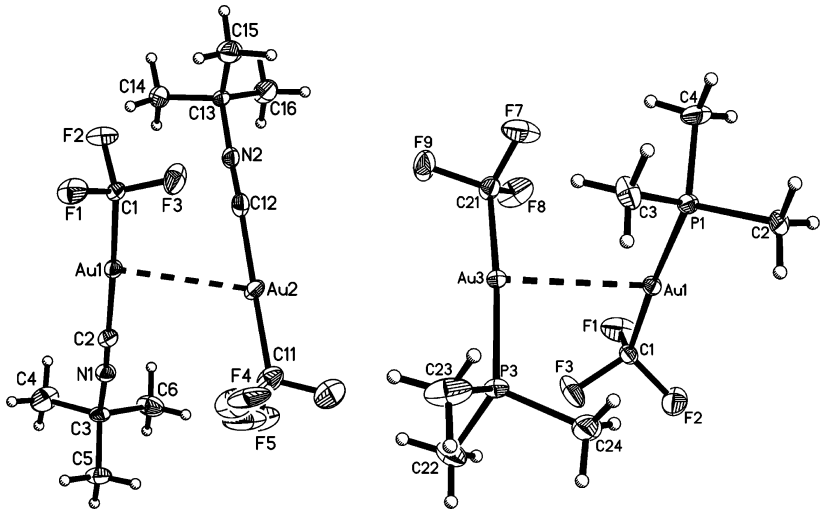

Figure 2. Molecular structures of complexes **7** (left) and **9** (right) showing the formation of aurophilic dimers. Thermal ellipsoids have been drawn at 50% probability.

respectively), and the carbenic carbons of **1**, **16**, **17**, and **19** are deshielded with respect to their halogenated analogues [AuX(IPr)] (Cl: 175.7 ppm; Br: 179.0 ppm),[51] or [Au-Cl_3(IPr)] (Cl: 145.7 ppm;[50] Br: 146.2 ppm[72]). The CF_3 carbon is deshielded in the Au(I) complexes (δ 155.9−166.5 ppm) with respect to the Au(III) ones (δ 123.9−125.3 ppm).

In agreement with the *trans* configuration observed in the crystal structures, all ^{i}Pr groups appear equivalent in the ^{1}H NMR spectra of **16** and **17**. The same was observed for **18**, which suggests that this complex has also a *trans* configuration. According to its lower symmetry, complex **19** shows duplicated signals for the ^{i}Pr groups. The coupling constant between the carbenic carbon and the three fluorine nuclei of **19** is very similar to those of **16** and **17**, which suggests that, in complex **19**, the CF_3 group is disposed *trans* to the IPr ligand.

Crystal Structures. The crystal structures of complexes **3**, **4**, **5**, **7**, **9**, **13**, **14**·$(CH_2Cl_2)_{0.5}$, **15**, PPN[Au$(CF_3)(C_6F_5)$]·$(CH_2Cl_2)_{0.5}$, **16**, and **17** have been determined by single-crystal X-ray diffraction (Figures 1−6). Important bond distances and angles are displayed in Table 1. The coordination geometries are linear (Au(I) complexes), or square-planar (Au(III) complexes) with slight distortions. The Au−CF_3 distances are very similar for all Au(I) trifluoromethyl complexes containing carbene, isonitrile, or C_6F_5 ligands (2.031−2.046 Å), with the exception of complex **3**. In contrast, the PMe_3 and dppe complexes **9** and **13** show sligthly longer Au−C bond distances (2.056−2.075 Å). Similar distances have been reported for PPN[Au$(CF_3)_2$] (2.059, 2.073 Å),[35] [Au$(CF_3)(PPh_3)$] (2.045 Å),[73] and [Au(CF_3)(CO)] (2.047 Å).[37] In PPN[Au(CF_3)-(C_6F_5)], the Au−CF_3 and Au−C_6F_5 distances do not differ significantly. In the Au(III) complexes, the Au−CF_3 distance is considerably larger for the dibromo complex **17** than for the dichloro complex **16** (2.112 vs 2.052 Å)

The ADC ligands of complexes **14** and **15** adopt a planar disposition with the ^{t}Bu or Xy groups oriented away from the NEt_2 group to minimize steric repulsions (Figure 4).

Carbene complexes **3**, **4**, **5**, **14**, and **15** do not show aurophilic interactions, which can be attributed to the steric hindrance produced by the CF_3 and carbene ligands. Accordingly, the shortest distance between two Au centers (3.939 Å) is found in complex **5**, which contains the less bulky carbene ligand of the series. In contrast, the structures of **7** and **9** are composed of aurophilic dimers (Figure 2) with short Au···Au distances (3.1526 Å (**7**); 3.1020 and 3.1282 Å (**9**)). In these cases, the lower sterical demand of the isonitrile and PMe_3 ligands and the skew relative disposition of the interacting molecules allow a close approach between both Au centers, while minimizing the steric repulsions. Aurophilic interactions between two inversion related molecules of complex **13** give rise to the formation of cyclic dimers (Figure 3), where the mutually interacting P−Au−C units adopt a skew disposition (Au···Au distance: 3.2024 Å). Similar aurophilic dimers are also found in the crystal structures of complexes [$Au_2X_2(\mu$-dppe)] (X = Cl,[74,75] C_2Ph[76]).

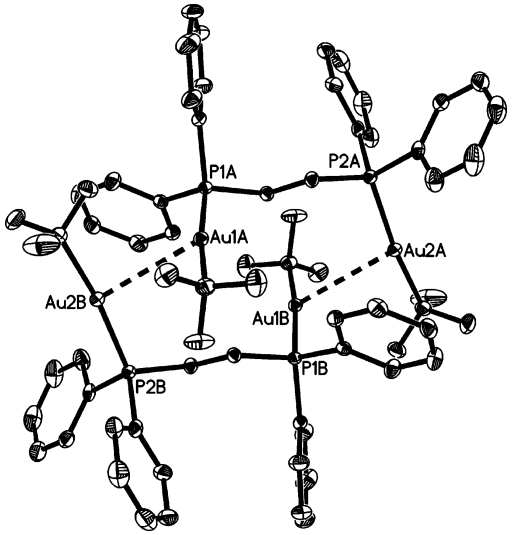

Figure 3. Molecular structure of complex **13** showing the formation of aurophilic cyclic dimers. Thermal ellipsoids have been drawn at 50% probability.

CONCLUSIONS

The reaction of Au(I) chloro complexes with AgF and $TMSCF_3$ allows the preparation of a wide range of Au(I) trifluoromethyl complexes in a single step from easily available Au(I) chloro complexes. By using this method, the first Au(I) trifluoromethyl complexes containing carbene ligands have

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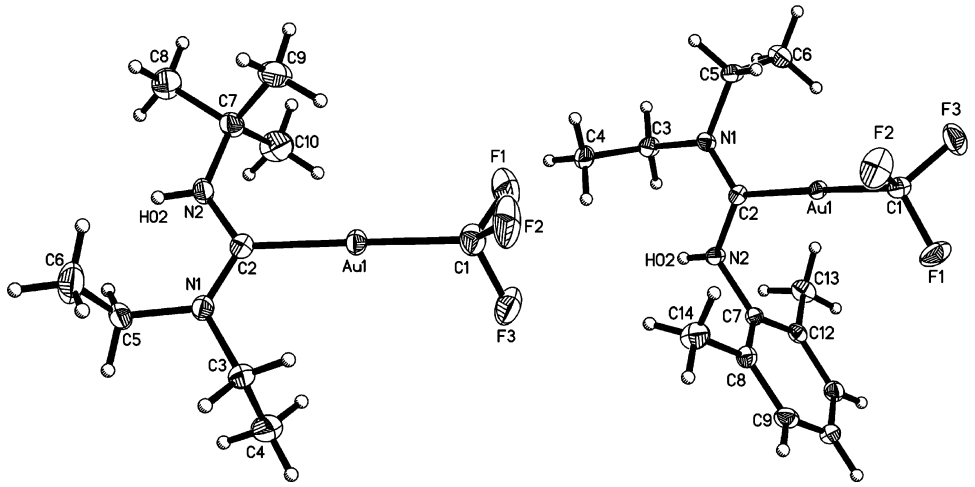

Figure 4. Molecular structures of complexes **14** (left) and **15** (right). Thermal ellipsoids have been drawn at 50% probability.

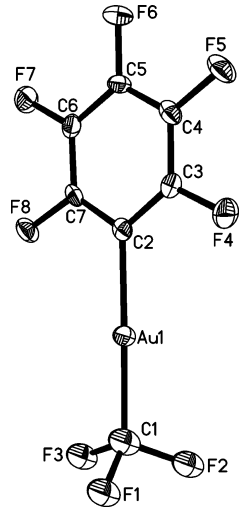

Figure 5. Molecular structure of the anion of the salt PPN[Au(CF_3)(C_6F_5)]. Thermal ellipsoids have been drawn at 50% probability.

been prepared, and representative examples of all synthesized types of complexes have been characterized by single-crystal X-ray diffraction.

Oxidation of [Au(CF_3)(IPr)] with Cl_2, Br_2, I_2, or ICl gives the corresponding square-planar Au(III) complexes, where the CF_3 and IPr ligands are disposed in a *trans* arrangement. *trans*-[Au(CF_3)I_2(IPr)] decomposes to [AuI(IPr)] and ICF_3 even at low temperature. In contrast, complexes *trans*-[Au(CF_3)-X_2(IPr)] (X = Cl, Br) are stable in solution in the dark, but reductively eliminate XCF_3 (X = Cl, Br) when irradiated with UV−visible light. Analogously, (*SP*-4-2)-[Au(CF_3)(Cl)(I)-(IPr)] reductively eliminates ICF_3, but not $ClCF_3$, under UV−visible irradiation. The observed behavior in the halotrifluoromethane elimination reactions is in agreement with a mechanism involving halide dissociation to give a cationic tricoordinate Au(III) intermediate [Au(CF_3)X(IPr)]Y, which undergoes reductive elimination to give [AuY(IPr)] and XCF_3. Studies of the synthesis of other types of Au(III) perfluoroalkylated complexes and the reductive elimination of perfluoroalkylated molecules are underway in our laboratories.

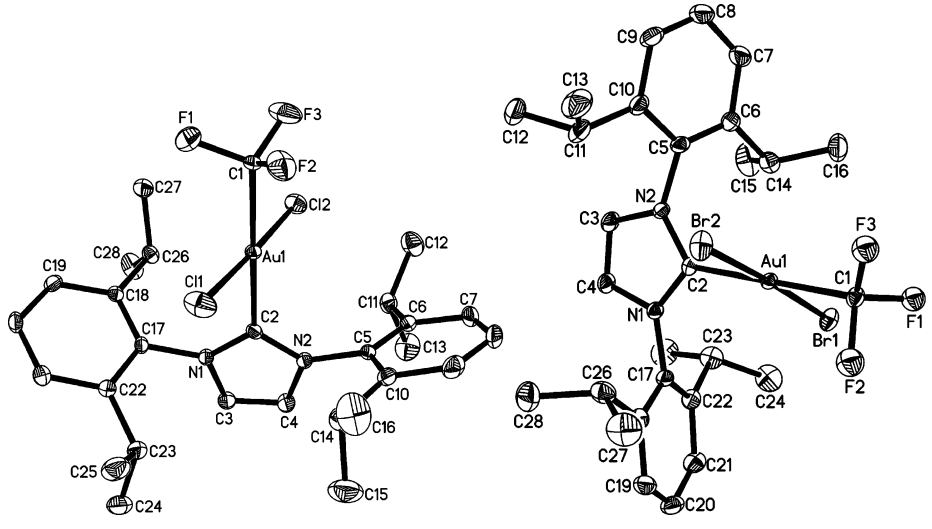

Figure 6. Molecular structures of complexes **16** (left) and **17** (right). Thermal ellipsoids have been drawn at 50% probability. Hydrogen atoms have been omitted for clarity.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes [Au(CF_3)L] and [Au(CF_3)X_2L]

L (Complex)	X	Au−CF_3	Au−L	E−Au−E′
IMes (**3**)[a]		2.013(13), 2.030(14)	Au−C: 2.041(8)	C−Au−C: 177.3(5), 176.0(5)
IBz (**4**)		2.039(3)	Au−C: 2.022(2)	C−Au−C: 177.80(9)
IBzMe (**5**)		2.041(3)	Au−C: 2.026(3)	C−Au−C: 175.82(12)
^{t}BuNC (**7**)		2.034(3), 2.031(4)	Au−C: 1.988(4), 1.996(4)	C−Au−C: 179.16(15), 177.44(13)
PMe_3 (**9**)		2.070(8), 2.056(8), 2.062(9)	Au−P: 2.291(2), 2.284(2), 2.290(2)	C−Au−P: 175.4(2), 175.9(2), 176.4(2)
1/2 dppe (**13**)		2.063(3), 2.075(3)	Au−P: 2.2960(7), 2.2895(7)	C−Au−P: 173.09(9), 173.96(9)
C(NH^{t}Bu)NEt_2 (**14**)		2.036(4)	Au−C: 2.048(3)	C−Au−C: 178.54(15)
C(NHXy)NEt_2 (**15**)		2.043(2)	Au−C: 2.043(2)	C−Au−C: 174.81(9)
C_6F_5[a]		2.044(8), 2.046(10)	Au−C: 2.047(3)	C−Au−C: 175.4(4), 177.9(3)
IPr (**16**)	Cl	2.086(3)	Au−C: 2.052(3), 2.059(3)	C−Au−C: 178.68(14), 179.83(17)
		2.085(4)	Au−Cl: 2.2650(8), 2.2816(9), 2.2716(9), 2.2763(9)	C_{NHC}−Au−Cl: 86.48(9), 93.87(9), 87.51(9), 92.33(9)
				C_{CF3}−Au−Cl: 92.24(10), 87.39, 92.34(13), 87.82(13)
				Cl−Au−Cl: 177.52(4), 179.75(4)
IPr (**17**)	Br	2.112(3)	Au−C: 2.073(2)	C−Au−C: 178.99(9)
			Au−Br: 2.4123(3), 2.4172(3)	C_{NHC}−Au−Br: 89.19(6), 89.83(7)
				C_{CF_3}−Au−Br: 91.51(6), 89.45(7)
				Br−Au−Br: 176.332(11)

[a]The CF_3 group is disordered over two positions.

EXPERIMENTAL SECTION

General Considerations. Complexes [AuCl(IPr)],[51] [AuI(SIPr)],[77] [AuI(IMes)],[51] [AuCl(IBz)],[78] [AuCl(IBzMe)],[79] [AuCl(I^{n}BuMe)],[49] [AuCl(PR_3)] (R = Ph, *p*-tolyl,[80] Me,[81] OMe[82]), [$(AuCl)_2$(*μ*-dppe)],[83] and [AuCl(CNR)] (R = ^{t}Bu,[84] Xy[68]) were prepared by reacting [AuCl(SMe_2)][85] with 1 equiv of the corresponding ligand in CH_2Cl_2 at room temperature. Other reagents were obtained from commercial sources and used without further purification. Commercial 2 M solutions of Me_3SiCF_3 in THF (Aldrich or Acros) were used. The trifluoromethylation reactions were carried out under a N_2 atmosphere using standard Schlenck techniques. Test reactions were performed in screw-cap NMR tubes equipped with a PTFE-covered rubber septum. EtCN was distilled over P_2O_5 and stored under N_2. CH_2Cl_2 was distilled over CaH_2.

Infrared spectra were recorded in the range of 4000−200 cm^{-1} with Nujol mulls between polyethylene sheets. ^{1}H NMR spectra were referenced to residual $CHDCl_2$ (5.32 ppm), $CHCl_3$ (7.24 ppm), and C_6D_5H (7.15 ppm). ^{19}F or ^{31}P{H} NMR spectra were referenced to external $CFCl_3$ or H_3PO_4 (0 ppm). ESI-MS and HR-MS spectra were measured using a solution of HCO_2H (1.01 mM) and $(NH_4)(HCO_2)$ (5 mM) in MeOH/H_2O (75:25 v:v) as carrier. Melting points were determined on a Reichert apparatus in an air atmosphere.

[AuI(IBz)]. NaI (180 mg, 1.20 mmol) was added to a solution of [AuCl(IBz)] (154 mg, 0.38 mmol) in MeCN (6 mL). After 1 h at room temperature, the mixture was evaporated under vacuum. The residue was extracted with 15 mL of CH_2Cl_2 and the extract was filtered through a Celite pad. The solution was concentrated under vacuum to ca. 1 mL. Addition of *n*-pentane (5 mL) gave a pale brown solid, which was filtered, washed with *n*-pentane (3 × 5 mL) and dried under vacuum. Yield: 156 mg, 83%. mp: 127−129 °C. Anal. Calcd for $C_{17}H_{16}AuIN_2$: C, 35.68; H, 2.82; N, 4.90. Found: C, 35.65; H, 2.94; N, 4.99. ^{1}H NMR (400.9 MHz, CD_2Cl_2): *δ* 7.36 (m, 10H, Ph), 6.92 (s, 2 H, imidazole), 5.41 (s, 4H, CH_2). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): *δ* 181.7 (CAu), 135.7 (*i*-Ph), 129.3 (Ph), 128.9 (Ph), 128.3 (Ph), 121.2 (CH imidazole), 55.0 (CH_2). (+)ESI-MS *m*/*z*: 462 ([Au(IBz)(NH_3)]$^+$), 573 (MH^+), 590 ([M + NH_4]$^+$), 693 ([Au$(IBz)_2$]$^+$), 1017 ([$Au_2(IBz)_2I$]$^+$).

[AuI(IBzMe)]. This was prepared in the same way as for [AuI(IBz)], starting from NaI (270 mg, 1.80 mmol) and [AuCl(IBzMe)] (305 mg, 0.58 mmol) in MeCN (6 mL). A pale brown solid was obtained. Yield: 316 mg, 95%. mp 159−161 °C. Anal. Calcd for $C_{11}H_{12}AuIN_2$: C, 26.63; H, 2.44; N, 5.65. Found: C, 26.73; H, 2.47; N, 5.59. ^{1}H NMR (400.9 MHz, CD_2Cl_2): *δ* 7.36 (m, 5H, Ph), 6.95 (d, $^3J_{HH}$ = 1.6 Hz, 1H, imidazole), 6.92 (d, 1H, $^3J_{HH}$ = 1.6 Hz, imidazole), 5.38 (s, 2H, CH_2), 3.85 (s, 3H, Me). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): *δ* 182.2 (CAu), 135.9 (*i*-Ph), 129.3 (Ph), 128.9 (Ph), 128.3 (Ph), 122.6 (CH imidazole), 120.7 (CH imidazole), 55.0 (CH_2), 38.2 (Me). (+)ESI-MS *m*/*z*: 497 (MH^+), 541 ([Au$(IBzMe)_2$]$^+$), 865 ([$Au_2(IBzMe)_2I$]$^+$).

[AuI(I^{n}BuMe)]. This was prepared in the same way as for [AuI(IBz)], starting from NaI (371 mg, 2.48 mmol) and [AuCl(I^{n}BuMe)] (294 mg, 0.79 mmol) in MeCN (6 mL). A pale brown solid was obtained. Yield: 264 mg, 72%. mp 97−99 °C. Anal. Calcd for $C_8H_{14}AuIN_2$: C, 20.79; H, 3.05; N, 6.06. Found: C, 20.79; H, 3.02; N, 6.11. ^{1}H NMR (400.9 MHz, CD_2Cl_2): *δ* 6.96 (d, $^3J_{HH}$ = 1.6 Hz, 1H, imidazole), 6.94 (d, $^3J_{HH}$ = 1.6 Hz, 1H, imidazole), 4.17 (t, $^2J_{HH}$ = 7.2 Hz, 2H, CH_2N), 3.82 (s, 3H, NMe), 1.83 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 1.38 (sept, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 0.96 (t, $^3J_{HH}$ = 7.2 Hz, 2H, Me). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): *δ* 181.5 (CAu), 121.9 (imidazole), 120.6 (imidazole), 51.0 (NCH_2), 38.1 (NMe), 33.3 (C2, ^{n}Bu), 19.9 (C3, ^{n}Bu), 13.7 (s, Me). (+)ESI-MS *m*/*z*: 363 ([Au(CO)(I^{n}BuMe)]$^+$), 463 (MH^+), 473 ([Au(I^{n}BuMe)$_2$]$^+$), 480 ([M + NH_4]$^+$), 797 ([Au_2(I^{n}BuMe)$_2$I]$^+$)

[Au(CF_3)(IPr)] (1). Me_3SiCF_3 (1.58 mmol) was added to a suspension of AgF (40 mg, 0.32 mmol) in EtCN (3 mL). The mixture was stirred at room temperature for 1.5 h in the darkness. To the resulting suspension, [AuCl(IPr)] (196 mg, 0.31 mmol) and EtCN (3 mL) were added. The mixture was stirred for 17 h at room temperature in the darkness. The resulting dark gray suspension was brougth to dryness under vacuum. The residue was extracted with CH_2Cl_2 (20 mL), and the extract was chromatographed on a silica gel column using CH_2Cl_2/*n*-hexane (2:1) as eluent. The collected colorless fraction (R_f = 0.74) was concentrated to ca. 1 mL. Addition of *n*-pentane (5 mL) gave a white solid, which was washed with *n*-pentane (3 × 2 mL), and dried under vacuum. Yield: 125 mg, 61%. mp: 210 °C (d). Anal. Calcd for $C_{28}H_{36}AuF_3N_2$: C, 51.38; H, 5.54; N, 4.28. Found: C, 51.23; H, 5.39; N, 4.60. IR (Nujol, cm^{-1}): 1132, 971 *ν*(C−F). ^{1}H NMR (400.9 MHz, CD_2Cl_2): *δ* 7.56 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*-C_6H_3), 7.35 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-C_6H_3), 7.22 (s, 2H, imidazole), 2.55 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*Me_2), 1.33 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): *δ* 188.5 (q, $^3J_{CF}$ = 13.7 Hz, CAu), 162.6 (q, $^1J_{CF}$ = 345.4 Hz, CF_3), 146.1 (*o*-C_6H_3), 134.2 (*i*-C_6H_3), 130.9 (*p*-C_6H_3), 124.5 (*m*-C_6H_3), 124.0 (CH imidazole), 29.2 (s, $CHMe_2$), 24.5

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($CHMe_2$), 24.0 ($CHMe_2$). ^{19}F NMR: (188.3 MHz, CD_2Cl_2): δ −28.4 (s). (+)ESI-MS m/z: 635 ($[Au(CF_2)(IPr)]^+$), 647.

[Au(CF_3)(SIPr)] (2). Me_3SiCF_3 (1.04 mmol) and AgF (43 mg, 0.34 mmol) were added to a solution of [AuI(SIPr)] (144 mg, 0.23 mmol) in EtCN (6 mL). The mixture was stirred for 24 h at room temperature in the darkness. The resulting dark gray suspension was brought to dryness under vacuum, and the residue was extracted with CH_2Cl_2 (20 mL). The extract was filtered through a Celite pad, concentrated under vacuum to ca. 3 mL, and chromatographed on a silica gel column using CH_2Cl_2/*n*-hexane (1:1) as eluent. The collected colorless fraction (R_f = 0.48) was concentrated to ca. 1 mL. Addition of *n*-pentane (10 mL) gave a white solid, which was washed with *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 96 mg, 71%. mp: 218−220 °C. Anal. Calcd for $C_{28}H_{38}F_3AuN_2$: C, 51.22; H, 5.83; N, 4.27. Found: C, 51.00; H, 5.81; N, 4.25. IR (Nujol, cm^{-1}): 1131, 972 ν(C−F). ^1H NMR (400.9 MHz, CD_2Cl_2): δ 7.47 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-C_6H_3), 7.29 (d, $^3J_{HH}$ = 7.6 Hz, 4H, *m*-C_6H_3), 4.04 (s, 4H, imidazole), 3.06 (sept, $^3J_{HH}$ = 6.8 Hz, 4H, $CHMe_2$), 1.39 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CHMe_2$), 1.34 (d, $^3J_{HH}$ = 6.8 Hz, 12H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 209.2 (q, $^3J_{CF}$ = 13.3 Hz, N_2CAu), 162.7 (q, $^1J_{CF}$ = 345.8 Hz, CF_3), 147.2 (*o*-C_6H_3), 134.3 (*i*-C_6H_3), 130.2 (*p*-C_6H_3), 124.8 (*m*-C_6H_3), 54.3 (CH_2), 29.3 ($CHMe_2$), 25.1 ($CHMe_2$), 24.2 ($CHMe_2$). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −29.1 (s). (+)ESI-MS m/z: 637 ($[Au(CF_2)(SIPr)]^+$), 649.

[Au(CF_3)(IMes)] (3). This was prepared in the same way as for **2**, starting from Me_3SiCF_3 (1.30 mmol), AgF (50 mg, 0.39 mmol), and [AuI(IMes)] (144 mg, 0.23 mmol) in EtCN (6 mL). CH_2Cl_2/*n*-hexane (3:1) was used as eluent (R_f = 0.74). Yield: 35 mg, 25% (white solid). mp: 214−216 °C. Anal. Calcd for $C_{22}H_{24}AuF_3N_2$: C, 46.33; H, 4.24; N, 4.91. Found: C, 46.56; H, 4.13; N, 5.16. IR (Nujol, cm^{-1}): 1132, 1129, 1077, 1018, 978 ν(C−F). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.15 (s, 2H, imidazole), 7.08 (s, 4H, Ar), 2.38 (s, 6 H, *p*-Me), 2.13 (s, 12 H, *o*-Me). $^{13}C\{^1H\}$ NMR (100.8 MHz, CD_2Cl_2): δ 186.8 (q, $^3J_{CF}$ = 14.0 Hz, N_2CAu), 162.9 (q, $^1J_{CF}$ = 345.2 Hz, CF_3), 140.2 (Ar), 135.2 (Ar), 135.0 (Ar), 129.6 (Ar), 123.1 (Ar), 21.3 (*p*-Me), 17.9 (*o*-Me). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ −28.5 (s). (+)ESI-MS m/z: 551 ($[Au(CF_2)(IMes)]^+$), 563.

[Au(CF_3)(IBz)] (4). This was prepared in the same way as for **2**, starting from Me_3SiCF_3 (1.26 mmol), AgF (53 mg, 0.42 mmol), and [AuI(IBz)] (153 mg, 0.25 mmol) in EtCN (6 mL). Reaction time: 20 h. CH_2Cl_2/*n*-hexane (3:1) was used as eluent (R_f = 0.60). Yield: 45 mg, 35% (white solid). mp: 138−140 °C. Anal. Calcd for $C_{18}H_{16}AuF_3N_2$: C, 42.04; H, 3.14; N, 5.45. Found: C, 41.86; H, 3.07; N, 5.40. IR (Nujol, cm^{-1}): 1132, 1017, 994, 950 ν(C−F). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.37 (m, 10H, Ph), 6.93 (s, 2H, imidazole), 5.39 (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 185.2 (q, $^3J_{CF}$ = 14.4 Hz, N_2CAu), 163.8 (q, $^1J_{CF}$ = 344.8 Hz, CF_3), 135.9 (Ph), 129.4 (Ph), 129.0 (Ph), 128.3 (Ph), 121.7 (CH imidazole), 55.2 (CH_2). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ −28.5 (s). (+)ESI-MS m/z: 473 ($[Au(CO)(IBz)]^+$), 495 ($[Au(CF_2)(IBz)]^+$), 507 ($[Au\{CF(OMe)\}(IBz)]^+$).

[Au(CF_3)(IBzMe)] (5). This was prepared in the same way as for **4**, starting from Me_3SiCF_3 (1.08 mmol), AgF (45 mg, 0.35 mmol), and [AuI(IBzMe)] (106 mg, 0.21 mmol) in EtCN (6 mL). Yield: 29 mg, 31% (white solid). mp: 130−132 °C. Anal. Calcd for $C_{12}H_{12}F_3AuN_2$: C, 32.89; H, 2.76; N, 6.39. Found: C, 32.56; H, 2.67; N, 6.27. IR (Nujol, cm^{-1}): 1134, 1119, 1018, and 965 ν(C−F). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.36 (m, 5H, Ph), 6.95 (d, 1H, $^3J_{HH}$ = 1.5 Hz, imidazole), 6.93 (d, 1H, $^3J_{HH}$ = 1.5 Hz, imidazole), 5.36 (s, 2H, CH_2), 3.86 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 185.3 (q, $^3J_{CF}$ = 14.6 Hz, N_2CAu), 164.1 (q, $^1J_{CF}$ = 344.5 Hz, CF_3), 136.1 (Ph), 129.3 (Ph), 128.9 (Ph), 128.3 (Ph), 122.9 (CH imidazole), 121.1 (CH imidazole), 54.9 (CH_2), 38.2 (Me). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ −28.6 (s). (+)ESI-MS m/z: 397 ($[Au(CO)(IBzMe)]^+$), 419 ($[Au(CF_2)(IBzMe)]^+$), 431($[Au\{CF(OMe)\}(IBzMe)]^+$).

[Au(CF_3)(I^{n}BuMe)] (6). This was prepared in the same way as for **2**, starting from Me_3SiCF_3 (1.77 mmol), AgF (69 mg, 0.54 mmol), and [AuI(I^{n}BuMe)] (160 mg, 0.35 mmol) in EtCN (6 mL). CH_2Cl_2/*n*-hexane (3:1) was used as eluent (R_f = 0.70). Yield: 71 mg, 51% (colorless oil). Anal. Calcd for $C_9H_{14}AuF_3N_2$: C, 26.74; H, 3.49, N, 6.93. Found: C, 26.87; H, 3.58; N, 6.79. IR (cm^{-1}): 1126, 1082, 975 ν(C−F). ^1H NMR (400.9 MHz, CD_2Cl_2): δ 6.97 (d, 1H, $^3J_{HH}$ = 1.6 Hz, imidazole), 6.94 (d, 1H, $^3J_{HH}$ = 1.6 Hz, imidazole), 4.17 (t, $^2J_{HH}$ = 7.2 Hz, 2H, CH_2), 3.84 (s, 3H, NMe), 1.86 (quint, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 1.38 (sext, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 0.98 (t, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 184.9 (q, $^3J_{CF}$ = 14.5 Hz, N_2CAu), 164.3 (q, $^1J_{CF}$ = 345.1 Hz, CF_3), 122.4 (CH imidazole), 121.1 (CH imidazole), 51.1 (C1, ^{n}Bu), 38.2 (NMe), 33.6 (C2, ^{n}Bu), 19.9 (C3, ^{n}Bu), 13.7 (C4, ^{n}Bu). ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ −28.4 (s). (+)ESI-MS m/z: 363 ($[Au(CO)(I^nBuMe)]^+$), 385 ($[Au(I^nBuMe)(CF_2)]^+$), 397 ($[Au\{CF(OMe)\}(I^nBuMe)]^+$).

[Au(CF_3)(CN^{t}Bu)] (7).[36] This was prepared in the same way as for **2**, starting from Me_3SiCF_3 (4.20 mmol), AgF (160 mg, 1.26 mmol), and [AuCl(CN^{t}Bu)] (262 mg, 0.83 mmol), in EtCN (10 mL). The compound was purified by chromatography on a silica gel column using acetone as eluent (R_f = 0.70), and the eluate was concentrated up to ca. 2 mL. After addition of CH_2Cl_2 (10 mL), the solution was stirred with $MgSO_4$ for 5 min and then filtered. The filtrate was evaporated to ca. 0.5 mL under vacuum, and *n*-hexane (10 mL) was added. The resulting white solid was washed with *n*-hexane (3 × 2 mL) and dried under vacuum. Yield: 205 mg, 71%. Anal. Calcd for $C_6H_9AuF_3N$: C, 20.64; H, 2.60; N, 4.01. Found: C, 20.95; H, 2.52; N, 4.01. IR (Nujol, cm^{-1}): 2249 ν(C≡N), 1136, 993 ν(C−F). ^1H NMR (400.9 MHz, $CDCl_3$): δ 1.55 (s, 9 H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 155.9 (q, $^1J_{CF}$ = 340.4 Hz, CF_3), 145.0 (q, $^3J_{FC}$ = 19.8, C≡N), 58.9 (s, CMe_3), 29.7 (s, CMe_3). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −29.6 (s, CF_3). (+)ESI-MS m/z: 252, 274, 286, 330 ($[Au(CF_2)(^t$BuNC$)]^+$), 372 (MNa^+).

[Au(CF_3)(CNXy)] (8). This was prepared in the same way as for **7**, starting from Me_3SiCF_3 (1.60 mmol), AgF (62 mg, 0.49 mmol), and [AuCl(CNXy)] (114 mg, 0.31 mmol) in EtCN (5 mL). Reaction time: 16 h. Yield: 53 mg, 43% (white solid). mp: 148−150 °C. Anal. Calcd for $C_{10}H_9AuF_3N$: C, 30.24; H, 2.28; N, 3.53. Found: C, 30.04; H, 2.22; N, 3.66. IR (Nujol, cm^{-1}): 2215 ν(C≡N), 1130, 995 ν(C−F). ^1H NMR (300.1 MHz, $CDCl_3$): δ 7.34 (t, $^3J_{HH}$ = 7.2 Hz, 1H, *p*-C_6H_3), 7.17 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-C_6H_3), 2.43 (s, 6H, Me). $^{13}C\{^1H\}$ NMR (100.8 MHz, $CDCl_3$): δ 157.8 (m, C≡N), 156.0 (q, $^1J_{CF}$ = 340.6 Hz, CF_3), 136.4 (*o*-C_6H_3), 131.3 (*p*-C_6H_3), 128.5 (*m*-C_6H_3), 123.8 (t, $^1J_{CN}$ = 13.5 Hz, *i*-C_6H_3), 14.1 (Me). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −29.5 (s, CF_3). (+)ESI-MS m/z: 356 ($[Au(CO)(XyNC)]^+$), 378 ($[Au(CF_2)(XyNC)]^+$), 390 ($[Au\{CF(OMe)\}(XyNC)]^+$), 402 ($[Au\{C(OMe)_2\}(XyNC)]^+$). Spectroscopic data of $[Au(CNXy)_2][Au(CF_3)_2]$ in the reaction crude: ^1H NMR (400.9 MHz, $CDCl_3$): δ 7.31 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-C_6H_3), 7.15 (d, 2H, *m*-C_6H_3), 2.47 (s, 6H, Me). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −26.9. (+)ESI-MS m/z: 459 ($[Au(CNXy)_2]^+$); (−)ESI-MS m/z: 235 ($[AuF_2]^-$), 285 ($[AuF(CF_3)]^-$), 335 ($[Au(CF_3)_2]^-$), 497.

[Au(CF_3)(PMe_3)] (9).[29,30,34] Me_3SiCF_3 (1.60 mmol) and AgF (60 mg, 0.47 mmol) were added to a solution of [AuCl(PMe_3)] (119 mg, 0.31 mmol) in EtCN (6 mL). The mixture was stirred for 24 h at room temperature in the darkness. The resulting dark gray suspension was brought to dryness under vacuum. The mixture was extracted with CH_2Cl_2 (20 mL), and the extract was filtered through a Celite pad, concentrated under vacuum to ca. 3 mL, and chromatographed. The crude product was a 5:1 mixture of **9** and $[Au(PMe_3)_2][Au(CF_3)_2]$. Pure **9** was obtained by column chromatography on a silica gel column using acetone/*n*-hexane (1:2) as eluent (R_f = 0.43). The eluate was concentrated up to ca. 2 mL. After addition of CH_2Cl_2 (10 mL), the solution was stirred with $MgSO_4$ for 5 min and then evaporated to ca. 0.5 mL under vacuum. Addition of *n*-hexane (10 mL) precipitated a white solid, which was filtered, washed with *n*-hexane (3 × 2 mL), and dried under vacuum. Yield: 58 mg, 55%. ^1H NMR (200.1 MHz, $CDCl_3$): δ 1.49 (d, 9 H, $^2J_{HP}$ = 10.2 Hz). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −30.5 (d, $^3J_{FP}$ = 49.1 Hz, CF_3). $^{31}P\{^1H\}$ NMR (162.3 MHz, $CDCl_3$): δ −0.30 (q, $^3J_{PF}$ = 49.0 Hz). Spectroscopic data of $[Au(PMe_3)_2][Au(CF_3)_2]$ in the reaction crude: ^1H NMR (300.1 MHz, $CDCl_3$): δ 1.65 (vt, 18 H, *N* = 8.1 Hz). ^{19}F NMR: (282.4 MHz, $CDCl_3$): δ −26.1 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 3.9 (s). (+)ESI-MS m/z: 349 ($[Au(PMe_3)_2]^+$); (−)ESI-MS m/z: 335 ($[Au(CF_3)_2]^-$).

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[Au(CF$_3$)(PPh$_3$)] (10).[30,34] This was prepared in the same way as for **9**, starting from Me_3SiCF_3 (1.14 mmol), AgF (43 mg, 0.34 mmol), and [AuCl(PPh$_3$)] (111 mg, 0.22 mmol) in EtCN (7 mL). R_f = 0.49. Yield: 70 mg, 59% (white solid). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.49 (m, 15 H, Ph). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −29.9 (d, $^3J_{FP}$ = 45.0 Hz, CF_3). ^{31}P{^{1}H} NMR (162.29 MHz, $CDCl_3$): δ 38.7 (q, $^3J_{PF}$ = 44.8 Hz).

[Au(CF$_3$){P(*p*-Tol)$_3$}] (11). This was prepared in the same way as for **9**, starting from Me_3SiCF_3 (1.40 mmol), AgF (53 mg, 0.42 mmol), and [AuCl{P(*p*-Tol)$_3$}] (143 mg, 0.27 mmol) in EtCN (6 mL). Reaction time = 20 h. R_f = 0.58. Yield: 119 mg, 78% (white solid). mp: 193−195 °C. Anal. Calcd for $C_{22}H_{21}AuF_3P$: C, 46.33; H, 3.71. Found: C, 46.03; H, 3.54. IR (Nujol, cm^{-1}): 1127, 994 ν(C−F). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ 7.36 (m, 6 H, C_6H_4), 7.25 (m, 6H, C_6H_4), 2.38 (s, 9 H, CH_3). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$): 166.3 (dq, $^1J_{CF}$ = 353.7 Hz, $^2J_{CP}$ = 180.4 Hz, CF_3), 142.2 (s, *p*-C_6H_4), 134.1 (d, $^2J_{CP}$ = 13.4 Hz, *o*-C_6H_4), 130.0 (d, $^3J_{CP}$ = 11.1 Hz, *m*-C_6H_4), 126.1 (d, $^1J_{CP}$ = 56.9 Hz, *i*-C_6H_4), 21.5 (s, Me).^{19}F NMR (188.3 MHz, $CDCl_3$): δ −29.9 (d, $^3J_{FP}$ = 44.8 Hz, CF_3). ^{31}P{^{1}H} NMR (162.3 MHz, $CDCl_3$): δ 36.8 (q, $^3J_{PF}$ = 44.8 Hz). (+)ESI-MS *m*/*z*: 501 ([Au{(P(*p*-Tol)$_3$}]$^+$), 551 ([Au(CF$_2$){(P(*p*-Tol)$_3$}]$^+$), 563 ([Au{CF(OMe)}{(P-(*p*-Tol)$_3$}]$^+$).

[Au(CF$_3$){P(OMe)$_3$}] (12). This was prepared in the same way as for **7**, starting from Me_3SiCF_3 (2.20 mmol), AgF (88 mg, 0.69 mmol), and [AuCl{P(OMe)$_3$}] (155 mg, 0.43 mmol) in EtCN (6 mL). Reaction time: 20 h. CH_2Cl_2/*n*-hexane (1:1) was used as eluent (R_f = 0.55). Yield: 109 mg, 64% (white solid; it becomes purple at room temperature and was stored at −32 °C to avoid decomposition). mp: 52−54 °C. Anal. Calcd for $C_4H_9AuF_3O_3P$: C, 12.32; H, 2.33. Found: C, 12.29; H, 2.18. IR (Nujol, cm^{-1}): 1137, 1018, 968 ν(C−F). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.77 (d, 9H, $^2J_{PH}$ = 12.9 Hz, Me). ^{13}C{^{1}H} NMR (100.81 MHz, $CDCl_3$): δ 166.5 (dq, $^1J_{CF}$ = 350.9 Hz, $^2J_{CP}$ = 262.7 Hz, CF_3), 52.8 (s, Me). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −31.4 (d, $^3J_{FP}$ = 61.8 Hz, CF_3). ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 145.0 (q, $^3J_{PF}$ = 61.8 Hz). (+)ESI-MS *m*/*z*: 321 ([Au{P(OMe)$_3$}]$^+$), 349 ([Au(CO){P(OMe)$_3$}]$^+$) 371 ([Au(CF$_2$){P(OMe)$_3$}]$^+$), 383 ([Au{CF(OMe)}{P(OMe)$_3$}]$^+$).

[Au$_2$(CF$_3$)$_2$(μ-dppe)] (13). This was prepared in the same way as for **7**, starting from Me_3SiCF_3 (0.82 mmol), AgF (53 mg, 0.42 mmol), and [Au$_2$Cl$_2$(μ-dppe)] (100 mg, 0.12 mmol), in a 1:1 mixture of EtCN/CH_2Cl_2 (10 mL). Reaction time: 18 h. Acetone/*n*-hexane (1:2) was used as eluent (R_f = 0.31). Yield: 57 mg, 53% (white solid). mp: 240 °C (d). Anal. Calcd for $C_{28}H_{24}Au_2F_6P_2$: C, 36.15; H, 2.60. Found: C, 35.83; H, 2.62. IR (Nujol, cm^{-1}): 1125, 967 ν(C−F). ^{1}H NMR (400.9 MHz, $CDCl_3$): δ 7.63 (m, 8 H, Ph), 7.50 (m, 12 H, Ph), 2.61 (d, $^2J_{PH}$ = 1.6 Hz, 4 H, CH_2). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2): δ 133.7 (d, $^2J_{CP}$ = 13.7 Hz, *o*-Ph), 132.7 (s, *p*-Ph), 130.0 (d, $^2J_{CP}$ = 9.1 Hz, *m*-Ph), 128.7 (d, $^1J_{CP}$ = 52.4 Hz, *i*-Ph), 23.7 (d, $^1J_{CP}$ = 35.1 Hz, CH_2), the signal of CF_3 was not observed. ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −30.2 (vd, *J* = 45.2 Hz, CF_3). ^{31}P{^{1}H} NMR (162.3 MHz, $CDCl_3$): δ 35.9 (m). (+)ESI-MS *m*/*z*: 861 ([Au$_2$(CF$_3$)(dppe)]$^+$), 911 ([Au$_2$(CF$_3$)(CF$_2$)(dppe)]$^+$), 923 ([Au$_2$(CF$_3$){CF(OMe)}(dppe)]$^+$).

Reaction of PPN[AuCl(C$_6$F$_5$)] with AgF and Me_3SiCF_3. Me_3SiCF_3 (0.60 mmol) and AgF (24 mg, 0.19 mmol) were added to a solution of PPN[AuCl(C$_6$F$_5$)] (110 mg, 0.12 mmol) in EtCN (6 mL). The mixture was stirred for 27 h at room temperature and brought to dryness under vacuum. The residue was extracted with CH_2Cl_2 (15 mL), and the extract was filtered through a Celite pad and concentrated to ca. 1 mL under vacuum. Addition of *n*-hexane precipitated an oily residue, which was stirred at 0 °C until it became a white solid (83 mg). This solid contains a mixture of complexes PPN[Au(CF$_3$)$_x$(C$_6$F$_5$)$_{2-x}$] (x = 0, 1, 2) and PPN[Ag(CF$_3$)$_2$]. Single crystals of PPN[Au(CF$_3$)(C$_6$F$_5$)] were obtained by liquid diffusion between a CH_2Cl_2 solution of the isolated solid and *n*-hexane. ^{1}H NMR (200.1 MHz, $CDCl_3$): δ 7.66−7.41 (m, 30 H, PPN). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ −25.9 (two doublets, $^2J_{AgF}$ = 100.2 and 87.8 Hz, [Ag(CF$_3$)$_2$]$^-$), −26.7 (s, [Au(CF$_3$)(C$_6$F$_5$)]$^-$), −28.6 (s, [Au-(CF$_3$)$_2$]$^-$), −115.6 (m, *o*-F of [Au(C$_6$F$_5$)$_2$]$^-$), −116.0 (m, *o*-F of [Au(CF$_3$)(C$_6$F$_5$)]$^-$), −162.9 (t, *p*-F of [Au(CF$_3$)(C$_6$F$_5$)]$^-$), −163.5 (t, *p*-F of [Au(C$_6$F$_5$)$_2$]$^-$), −164.8 (m, *m*-F of [Au(CF$_3$)(C$_6$F$_5$)]$^-$ and [Au(C$_6$F$_5$)$_2$]$^-$). The signals of [Ag(CF$_3$)$_2$]$^-$ and [Au(CF$_3$)$_2$]$^-$ were assigned by comparison with reported values.[35,71] The signals of [Au(C$_6$F$_5$)$_2$]$^-$ were assigned by comparison with those of a sample of PPN[Au(C$_6$F$_5$)$_2$] prepared by a reported method.[86] ^{31}P{^{1}H} NMR (81.0 MHz, $CDCl_3$): δ 21.6 (s, PPN). (−)ESI-MS (MeCN) *m*/*z*: 242 ([AuF(CN)]$^-$), 285 ([AuF(CF$_3$)]$^-$), 335 ([Au(CF$_3$)$_2$]$^-$), 383 ([AuF-(C$_6$F$_5$)]$^-$), 390 ([Au(CN)(C$_6$F$_5$)]$^-$), 433 ([Au(CF$_3$)(C$_6$F$_5$)]$^-$), 531 ([Au(C$_6$F$_5$)$_2$]$^-$).

[Au(CF$_3$){(C(NH^{t}Bu)(NEt$_2$)}] (14). A solution of **7** (46 mg, 0.13 mmol) in $NHEt_2$ (2 mL) was stirred for 5 h at room temperature. The resulting colorless solution was evaporated to dryness under vacuum, and the residue was extracted with CH_2Cl_2 (10 mL). After filtration through Mg_2SO_4, the extract was concentrated under vacuum to ca. 0.5 mL. Addition of *n*-hexane precipitated a white solid, which was filtered, washed with *n*-hexane (2 × 2 mL), and dried under vacuum. The solid was stored at −32 °C because it slowly decomposes at room temperature. Yield: 28 mg, 50%. mp: 51−53 °C (dec). Anal. Calcd for $C_{10}H_{20}AuF_3N_2$: C, 28.45; H, 4.77; N, 6.63. Found: C, 28.24; H, 4.57; N, 6.68. IR (Nujol, cm^{-1}): 3377 ν(N−H), 1539 ν(C=N), 1120, 964 ν(C−F). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 5.80 (br s, 1H, NH), 3.93 (q, $^3J_{HH}$ = 7.1 Hz, 2H, C*H*$_2$Me), 3.22 (q, $^3J_{HH}$ = 7.3 Hz, 2H, C*H*$_2$Me), 1.60 (s, 9H, ^{t}Bu), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_2$*Me*), 1.15 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_2$*Me*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 204.1 (q, $^3J_{CF}$ = 12.8 Hz, N_2CAu), 162.2 (q, $^1J_{CF}$ = 346.5 Hz, CF_3), 54.1 (*C*H$_2$Me), 54.0 (*C*Me$_3$), 40.1 (*C*H$_2$Me), 31.9 (*C*Me$_3$), 14.8 (CH$_2$*Me*), 11.8 (CH$_2$*Me*). ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −27.5 (s, CF_3). (+)ESI-MS *m*/*z*: 381, 403 ([Au{C(NH^{t}Bu)(NEt$_2$)}(CF$_2$)]$^+$), 415 ([Au{C(NH^{t}Bu)(NEt$_2$)}(CF$_2$)]$^+$).

[Au(CF$_3$){(C(NHXy)(NEt$_2$)}] (15). This was prepared in the same way as for **14**, starting from **8** (50 mg, 0.13 mmol). The white solid was stored at −32 °C because it slowly decomposes to metallic gold at room temperature. Yield: 33 mg, 56%. mp: 119−121 °C (dec). Anal. Calcd for $C_{14}H_{20}AuF_3N_2$: C, 35.76; H, 4.29; N, 5.96. Found: C, 35.66; H, 4.16; N, 5.99. IR (Nujol, cm^{-1}): 3363, 3330 ν(N−H), 1543 ν(C=N), 1126, 975 ν(C−F). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.17−7.08 (m, 3H, Ar), 6.80 (br s, 1H, NH), 3.95 (q, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 3.44 (q, $^3J_{HH}$ = 7.2 Hz, 2H, CH_2), 2.23 (s, 6H, Me-Ar), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH$_2$*Me*), 1.32 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH$_2$*Me*). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 205.9 (q, $^3J_{CF}$ = 13.1 Hz, N_2CAu), 161.9 (q, $^1J_{CF}$ = 346.8 Hz, CF_3), 136.7 (s, *o*-C_6H_3), 136.2 (s, *p*-C_6H_3), 128.5 (s, *m*-C_6H_3), 52.6 (CH_2), 40.8 (CH_2), 19.0 (*Me*-Ar), 15.0 (CH$_2$*Me*), 12.4 (CH$_2$*Me*); the signal of C−N was not observed. ^{19}F NMR (282.4 MHz, $CDCl_3$): δ −28.0 (s, CF_3). (+)ESI-MS *m*/*z*: 451 ([Au{C-(NHXy)(NEt$_2$)}(CF$_2$)]$^+$), 463 ([Au{CF(OMe)}{C(NHXy)-(NEt$_2$)}]$^+$).

***trans*-[AuCl$_2$(CF$_3$)(IPr)] (16).** A solution of $PhICl_2$ (16 mg, 0.058 mmol) in CH_2Cl_2 (3 mL) was added to a solution of [Au(CF$_3$)(IPr)] (38 mg, 0.058 mmol) in CH_2Cl_2 (3 mL) at −90 °C. The reaction mixture was slowly warmed to room temperature over 2 h with stirring. The resulting pale yellow solution was evaporated to dryness under vacuum, and the residue was chromatographed on a silica gel column using CH_2Cl_2/*n*-hexane (2:1) as eluent. The collected colorless fraction (R_f = 0.76) was evaporated to dryness, and the residue was washed with *n*-hexane (5 mL), to give a white solid, which was dried under vacuum. Yield: 32 mg, 75%. mp: 265 °C (d). Anal. Calcd for $C_{28}H_{36}Cl_2F_3AuN_2$: C, 46.36; H, 5.00; N, 3.86. Found: C, 46.20; H, 5.00; N, 3.93. IR (Nujol, cm^{-1}): 1121, 1081, 1057, 1019 ν(C−F). ^{1}H NMR (400.9 MHz, CD_2Cl_2): δ 7.58 (t, $^3J_{HH}$ = 8.0 Hz, 2H, *p*-C_6H_3), 7.38 (d, $^3J_{HH}$ = 8.0 Hz, 4H, *m*-C_6H_3), 7.31 (s, 2H, imidazole), 2.82 (sept, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*Me$_2$), 1.37 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH*Me*$_2$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR (100.8 MHz, CD_2Cl_2): δ 165.5 (q, $^3J_{CF}$ = 29.5 Hz, N_2CAu), 146.4 (*o*-C_6H_3), 133.2 (*i*-C_6H_3), 131.5 (*p*-C_6H_3), 126.1 (CH imidazole), 125.3 (q, $^1J_{FC}$ = 358.5 Hz, CF_3), 124.8 (*m*-C_6H_3), 29.2 (*C*HMe$_2$), 26.5 (CH*Me*$_2$), 22.9 (CH*Me*$_2$). ^{19}F NMR (188.3 MHz, CD_2Cl_2): −32.4 (s). (+)ESI-MS *m*/*z*: 602 ([Au(NH$_3$)(IPr)]$^+$), 613 ([Au(CO)(IPr)]$^+$), 742 ([M + NH$_4$]$^+$).

***trans*-[AuBr$_2$(CF$_3$)(IPr)] (17).** A solution of Br_2 in CH_2Cl_2 (35 μL, 2.0 M, 0.07 mmol)) was added to a solution of [Au(CF$_3$)(IPr)] (30

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mg, 0.05 mmol) in CH_2Cl_2 (4 mL) at −90 °C. The reaction mixture was slowly warmed to room temperature over 2 h with stirring. The orange solution was evaporated to dryness, and the resulting yellow solid obtained was washed with *n*-hexane (5 mL) and dried under vacuum. Yield: 33 mg, 88%. mp: 268 °C (d). Anal. Calcd for $C_{28}H_{36}Br_2F_3AuN_2$: C, 41.30; H, 4.46; N, 3.44. Found: C, 41.46; H, 4.36; N, 3.65. IR (Nujol, cm^{-1}): 1109, 1075, 1054, 1019 ν(C−F). ^1H NMR (400.9 MHz, CD_2Cl_2): δ 7.58 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*-C_6H_3), 7.37 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-C_6H_3), 7.33 (s, 2H, imidazole), 2.95 (sept, $^3J_{HH}$ = 6.6 Hz, 4H, C*H*Me$_2$), 1.40 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2): δ 163.0 (q, $^3J_{CF}$ = 28.5 Hz, N_2CAu), 146.4 (*o*-C_6H_3), 133.6 (*i*-C_6H_3), 131.5 (*p*-C_6H_3), 126.4 (CH imidazole), 124.9 (*m*-C_6H_3), 123.9 (q, $^1J_{FC}$ = 356.6 Hz, CF_3), 29.3 (*C*HMe$_2$), 26.6 (CH*Me*$_2$), 23.2 (CH*Me*$_2$). ^{19}F NMR (188.3 MHz, CD_2Cl_2): −24.5 (s). (+)ESI-MS (condiciones) *m*/*z*: 602 ([Au(NH$_3$)(IPr)]$^+$), 613 ([Au(CO)(IPr)]$^+$), 832 ([M + NH$_4$]$^+$).

Reaction of 1 with I_2. A solution of **1** (8 mg, 0.01 mmol) in CD_2Cl_2 (0.5 mL) in an NMR tube was cooled to −90 °C. Then, a solution of I_2 (0.04 mmol) in CD_2Cl_2 (0.15 mL) was added slowly to avoid a temperature increase. After 5 min, the tube was inserted into the precooled (−80 °C) NMR probe. The ^1H and ^{19}F NMR spectra showed a 1.7:0.9:1:1 mixture of **1**, [$AuI_2(CF_3)$(IPr)], ICF_3, and [AuI(IPr)]. The temperature was gradually increased, and the composition of the reaction mixture was monitored by ^1H and ^{19}F NMR spectroscopy. After 2 h at room temperature, only [AuI(IPr)] and ICF_3 were observed. NMR data of the reaction products: (a) ***trans*-[$AuI_2(CF_3)$(IPr)]**, ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.56 (t, $^3J_{HH}$ = 7.6 Hz, 2H, *p*-C_6H_3), 7.38 (s, 2H, imidazole), 7.37 (d, $^3J_{HH}$ = 8.1 Hz, 4H, *m*-C_6H_3), 3.13 (sept, $^3J_{HH}$ = 6.7 Hz, 4H, C*H*Me$_2$), 1.43 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CH*Me*$_2$), 1.13 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH*Me*$_2$). ^{19}F NMR (282.4 MHz, CD_2Cl_2): −9.5 (s). (b) **[AuI(IPr)]**,[51] ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.58 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*-C_6H_3), 7.35 (d, $^3J_{HH}$ = 7.8 Hz, 4H, *m*-C_6H_3), 7.25 (s, 2H, imidazole), 2.56 (sept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*Me$_2$), 1.33 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH*Me*$_2$). **ICF_3** (see below).

(*SP*-4-2)-[Au(Cl)(I)(CF_3)(IPr)] (18). A solution of ICl in CH_2Cl_2 (67 μL, 0.048 mmol of ICl) was added to a solution of [Au(CF_3)(IPr)] (31 mg, 0.047 mmol) in CH_2Cl_2 (3 mL) at −70 °C. After 2 min, a layer of cold *n*-hexane (15 mL) was added carefully over the CH_2Cl_2 solution. Orange crystals formed after storing the two-layer solution at −32 °C for 3 days. The solvents were removed, and the crystals were dried under vacuum. Yield: 24 mg, 62%. mp: 183 °C (d). Anal. Calcd for $C_{28}H_{36}ClF_3IAuN_2$: C, 41.16; H, 4.44; N, 3.43. Found: C, 41.20; H, 4.32; N, 3.49. IR (Nujol, cm^{-1}): 1121, 1106, 1072, 1050, ν(C−F). ^1H NMR (300.1 MHz, CD_2Cl_2): δ 7.57 (t, $^3J_{HH}$ = 7.8 Hz, 2H, *p*-C_6H_3), 7.38 (d, $^3J_{HH}$ = 7.9 Hz, 2H, *m*-C_6H_3), 7.36 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-C_6H_3), 7.34 (s, 2H, imidazole), 2.98 (sept, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me$_2$), 2.97 (sept, $^3J_{HH}$ = 6.7 Hz, 2H, C*H*Me$_2$), 1.43 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 1.39 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 1.14 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH*Me*$_2$), 1.11 (d, $^3J_{HH}$ = 6.9 Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (150.9 MHz, CD_2Cl_2): δ 162.5 (q, $^3J_{CF}$ = 27.9 Hz, N_2CAu), 146.9 (*o*-C_6H_3), 145.9 (*o*-C_6H_3), 133.7 (*i*-C_6H_3), 131.5 (*p*-C_6H_3), 126.5 (CH imidazole), 125.0 (*m*-C_6H_3), 124.9 (*m*-C_6H_3), 124.0 (q, $^1J_{FC}$ = 354.6 Hz, CF_3), 29.6 (*C*HMe$_2$), 29.2 (*C*HMe$_2$), 26.7 (CH*Me*$_2$), 26.6 (CH*Me*$_2$), 23.6 (CH*Me*$_2$), 23.0 (CH*Me*$_2$). ^{19}F NMR (282.4 MHz, CD_2Cl_2): δ −21.5 (s). (+)ESI-MS *m*/*z*: 613 ([Au(CO)(IPr)]$^+$), 797 ([Au(Cl)(I)(CF_2)(IPr)]$^+$), 834 ([M + NH$_4$]$^+$).

Thermal and Photochemical Reactions of Complexes 16, 17, and 18. Solutions of the complexes (6−8 mg) in CD_2Cl_2 (0.5 mL) in NMR tubes were (a) heated to 80 °C for 16 h (**16** and **17**), or (b) irradiated at room temperature for 60 min (**16** and **17**) or 30 min (**19**) with a medium-pressure 150 W Hg lamp, using an aqueous solution of KI (1%) as a cutoff filter (λ > 260 nm). The course of the reactions was monitored by ^1H NMR spectroscopy. ^{19}F NMR data of the detected halotrifluoromethanes (CD_2Cl_2, δ): $ClCF_3$, −28.1; $BrCF_3$, −18.2; ICF_3, −5.7. These values agree with those reported.[87]

X-ray Crystallography. Crystals of compounds **3**, **4**, **5**, **7**, **9**, **13**, **14**·$(CH_2Cl_2)_{0.5}$, **15**, PPN[Au(CF_3)(C_6F_5)]·$(CH_2Cl_2)_{0.5}$, **16**, and **17** were obtained by liquid diffusion between a CH_2Cl_2 solution and *n*-hexane and measured on a Bruker D8 QUEST machine at 100 K. Data were collected using a high brilliance microfocus sealed tube with Mo−Kα radiation (0.71073 Å) in ω-scan. The structures were solved by direct methods. All were refined anisotropically on F^2. The hydrogen in the NH units of **16** was refined freely with DFIX. The ordered methyl groups were refined using rigid groups and the other hydrogens were refined using a riding mode. Special features: In complexes **3**, PPN[Au(CF_3)(C_6F_5)]·$(CH_2Cl_2)_{0.5}$, and **17**, the CF_3 group is disordered over two positions. The relative occupances of each position are 53:47, 57:43, and 55:45, respectively. In **7**, two fluorine atoms of the CF_3 group are disordered over two positions with a relative occupance of 50:50. In **14**·$(CH_2Cl_2)_{0.5}$, the CH_2Cl_2 molecule is disordered over an inversion center and its hydrogen atoms were not included in the refinement. In compound **16**, the highest residual electron density is a peak of 5.44 e/Å^3 at 0.92 Å from C33. Different crystals were measured, and all of them gave the same peak at the same position, which suggest that this peak could be originated by a small amount of twinning that could not be solved.

■ ASSOCIATED CONTENT

Supporting Information

Additional spectroscopic data, tables with relevant crystallographic data, and CIF files are supplied as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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