(CF₃)₃Au as a Highly Acidic Organogold(III) Fragment

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Dedicated to Professor Juan Forniés on the occasion of his 70th birthday

Abstract: The Lewis acidity of perfluorinated trimethylgold, (CF₃)₃Au, has been assessed by theoretical and experimental methods. It has been found that the (CF₃)₃Au unit is much more acidic than its non-fluorinated homologue (CH₃)₃Au, probably setting the upper limit in the acidity scale for any neutral R₃Au organogold(III) species. The significant acidity increase upon fluorination is in line with the CF₃ group being in fact more electron-withdrawing than CH₃. The solvate (CF₃)₃Au·OEt₂ (**1**) is presented as a convenient synthon of the unsaturated, 14-electron species (CF₃)₃Au. Thus, the weakly coordinated ether molecule in **1** is readily replaced by a variety of neutral ligands affording a wide range of (CF₃)₃AuL compounds, which have been isolated and conveniently characterized. Most of these mononuclear compounds exhibit marked thermal stability. This enhanced stabilization can be rationalized in terms of substantially stronger [Au]–L interactions with the (CF₃)₃Au unit. An affinity scale of this single-site, highly acidic organogold(III) fragment has been calculated by DFT methods and experimentally mapped for various neutral monodentate ligands. The high-energy profile calculated for the fluorotropic [Au]–CF₃ ⇌ F–[Au]←CF₂ process makes this potential decomposition path unfavorable and adds to the general stabilization of the fragment.

Introduction

Strong Lewis acids are fascinating chemical species, which are eagerly sought because of their interesting and sharp reactivity.^[1–5] Prototypical examples of strong Lewis acids in organic chemistry are carbocations, R₃C⁺. These highly reactive, unsaturated species were first formulated as ephemeral intermediates, but were unambiguously identified by the late Nobel laureate G. Olah and his coworkers.^[6] Isoelectronic with charged carbocations, R₃C⁺, are neutral boranes, R₃B, whose Lewis-acidic properties have also been thoroughly studied and vastly exploited.^[7] Their use as promoters in alkene polymerization processes catalyzed by alkyl metallocenes has fostered a rapid and fruitful development of an astonishing variety of boranes.^[8]

In the search for ever stronger Lewis-acidic boranes, R₃B, it

was soon realized that fluorination of the organic group R resulted in enhancement of the Lewis acidity in the corresponding R^F₃B derivatives.^[9–11] In fact, the most widely used borane is by far (C₆F₅)₃B, which exhibits a considerable Lewis acidity.^[12] The perfluoromethyl-derivative (CF₃)₃B would be expected to exhibit even stronger Lewis acidity. Although this compound has not yet been isolated as such, its derivatives (CF₃)₃B·L^[13] and, especially the singular carbonyl compound (CF₃)₃BCO,^[14] evidence a greatly enhanced acidity of the (CF₃)₃B moiety.^[15,16]

The trifluoromethyl group, CF₃, exhibits properties departing so markedly from those of non-fluorinated methyl, CH₃, that T. Ritter has suggested that it be considered "more appropriately as a distinct functional group" rather than just as a substituted methyl group.^[17] It has traditionally been considered^[18] as a compact, electron-withdrawing group with an electronegativity value (χ_{CF₃} = 3.49)^[19] virtually identical to that of chlorine (χ_{Cl} = 3.48)^[19] and additionally exhibiting a high *trans* influence in its transition-metal compounds.^[20] Recently, it has also been considered as a σ non-innocent ligand able to induce inversion in the ligand-field splitting of metal d orbitals, especially in late transition metals, as in the homoleptic [(CF₃)₄Cu][–] anion.^[21] With regard to gold chemistry, the CF₃ group was first introduced by Puddephatt in the 70s.^[22] Since that early work, the study of trifluoromethyl-gold derivatives has aroused continued interest, but only recently has developed into a hot research topic.^[23]

We have recently found a convenient entry to the chemistry of the (CF₃)₃Au fragment, which has emerged as a stereochemically robust moiety with a marked reluctance to undergo reductive elimination of CF₃–CF₃.^[24] The anionic derivatives [PPh₄][(CF₃)₃AuX] (X = F, Cl, Br, I, CN) have also been isolated and conveniently characterized. We wanted now to assess the Lewis acidity of the (CF₃)₃Au unit in comparison with that of its non-fluorinated homologue (CH₃)₃Au in order to establish the effect of fluorination. To this aim, a combined theoretical and experimental approach has been used. Further comparison with the isoelectronic (CF₃)₃B species as well as with the ubiquitous (C₆F₅)₃B derivative provides parallels between transition-metal and main-group chemistry, bridging what might otherwise appear to be a conceptual divide.^[21,25]

Results and Discussion

The naked (CF₃)₃Au species seems to have been prepared by Lagow and his coworkers^[26] as the result of gas-phase reaction of Au vapors with CF₃· radicals and subsequent matrix isolation [Eq. (1)].

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This procedure requires highly specialized and rather expensive equipment that cannot be afforded by most chemistry laboratories. Moreover, naked $(\text{CF}_3)_3\text{Au}$ is thermally unstable and is produced just in modest yield (~20%) as estimated by derivatization. We sought to circumvent all these drawbacks by preparing a $(\text{CF}_3)_3\text{Au}\cdot\text{L}$ adduct formed with a weakly coordinating ligand L. The ligand of choice was Et_2O , as already used by Gilman and Woods to stabilize the non-fluorinated homologue, $(\text{CH}_3)_3\text{Au}$.^[27]

Synthesis of the etherate $(\text{CF}_3)_3\text{Au}\cdot\text{OEt}_2$ (1): By room-temperature treatment of the iodo-derivative $[\text{PPh}_4][(\text{CF}_3)_3\text{Au}]$ ^[24] with the equimolar amount of AgClO_4 in a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture, precipitation of AgI is observed with concomitant formation of the solvento complex $(\text{CF}_3)_3\text{Au}\cdot\text{OEt}_2$ (1) in solution (Scheme 1). Solutions of the etherate 1 can be freed from the accompanying $[\text{PPh}_4]\text{ClO}_4$ salt by replacing the initial solvent mixture with a new one consisting of $\text{Et}_2\text{O}/n$ -hexane in 1:3 volume ratio and allowing it to stand at -80°C overnight. Once filtered, colorless solutions of 1 are reasonably stable at room temperature if protected from the action of light. These solutions are free from byproducts and are found to be appropriate as such for most synthetic purposes. It is interesting to note that compound 1 shows greatly enhanced thermal stability relative to the homologous non-fluorinated etherate, $(\text{CH}_3)_3\text{Au}\cdot\text{OEt}_2$, which already decomposes at about -40°C in Et_2O solution giving a gold mirror and a mixture of ethane and methane.^[27]

Scheme 1. Synthetic method to prepare the etherate $(\text{CF}_3)_3\text{Au}\cdot\text{OEt}_2$ (1).

The room-temperature ^{19}F NMR spectrum of 1 shows two broad bands at ca. -25 and -39 ppm in 1:2 integrated ratio that are resolved at low temperature into a septet and a quartet, respectively. This behavior indicates that the Et_2O ligand is labile and undergoes rapid exchange at room temperature. In fact, even small amounts of free Et_2O in the sample result in broadening of the signal without noticeable shift in the corresponding δ_{F} values. Although we tried to isolate compound 1 as a pure substance, its marked hygroscopic character together with its high solubility in Et_2O and n -hexane even at low temperatures, rendered our task difficult. After evaporation of ethereal solutions of 1 to dryness at 0°C , followed by extraction of the residue in n -hexane, and crystallization at -80°C , a deliquescent white solid was eventually obtained that melted just above 0°C .^[28] The ^{19}F NMR spectrum of this solid in CD_2Cl_2 solution at -60°C (Figure 1a) is consistent with that observed in the initial reaction medium (Scheme 1) with just a slight shift in δ_{F} values being attributable to the different dielectric constant of

the solvent used in each case ($\text{Et}_2\text{O}/n$ -hexane vs. CD_2Cl_2). In the ^1H NMR spectrum (Figure 1b), the signals due to coordinated Et_2O ($\delta_{\text{H}} = 4.05$ (CH_2) and 1.52 (CH_3) ppm) appear downfield shifted with respect to those of the free molecule ($\delta_{\text{H}} = 3.43$ (CH_2) and 1.15 (CH_3) ppm in CD_2Cl_2 solution),^[29] the corresponding protons being therefore deshielded upon coordination to the acidic $(\text{CF}_3)_3\text{Au}$ fragment (Table 1). Similarly deshielded signals were also found in oxonium $[\text{H}(\text{OEt}_2)_2]^+$ salts of weakly coordinating anions^[30] as well as in the related perfluorophenyl derivative, $(\text{C}_6\text{F}_5)_3\text{Au}\cdot\text{OEt}_2$.^[31] There is therefore strong spectroscopic evidence suggesting that the solid samples obtained consist mainly of compound 1. However, such samples always contained variable amounts of free Et_2O (see marked signals in Figure 1b) that could not be completely removed without altering the integrity of the main component. This failure eventually defeated our repeated efforts to isolate compound 1 in analytically pure form. The fact that two separate sets of signals are observed for coordinated and free Et_2O in the ^1H NMR spectrum at -60°C (Figure 1b) indicates that exchange between them has been sufficiently slowed down at that temperature.

Figure 1. ^{19}F (a) and ^1H (b) NMR spectra of the etherate 1 in CD_2Cl_2 solution at -60°C with relevant parameters indicated. The signals marked with an asterisk correspond to free Et_2O .^[29]

Table 1. Relevant NMR parameters corresponding to the neutral (CF₃)₃AuL derivatives.^[a]

Compound	$\delta_F(q)^{[b]}$	$\delta_F(spt)^{[c]}$	$^4J(F,F)^{[d]}$	Other NMR signals
(CF ₃) ₃ Au(OEt ₂) (1) ^[e]	-38.81	-25.27	6.1	$\delta_H = 4.05$ (q, $^3J(H,H) = 7.1$; CH ₂), 1.52 (t, CH ₃)
(CF ₃) ₃ Au(CNtBu) (2)	-29.39	-32.07	6.3	$\delta_H = 1.63$ (s)
(CF ₃) ₃ Au(NCMe) (3) ^[e]	-35.76	-27.48	6.3	$\delta_H = 2.52$ (s)
(CF ₃) ₃ Au(py) (4) ^[f]	-37.85	-28.89	6.5	$\delta_H = 8.55$ (m _c , 2H; H ^o), 8.14 (tt, 1H; H ^p), 7.74 (m _c , 2H; H ^m)
(CF ₃) ₃ Au(PMe ₃) (5) ^[g]	-30.67	-32.41	6.5	$\delta_P = 3.09$ [qspt, $^3J(F,P) = 78.8$ (<i>trans</i>), $^3J(F,P) = 10.6$ (<i>cis</i>)]; $\delta_H = 1.78$ [d, $^2J(H,P) = 12.5$]
(CF ₃) ₃ Au(PPh ₃) (6)	-30.63	-31.19	7.4	$\delta_P = 27.90$ [qspt, $^3J(F,P) = 78.7$ (<i>trans</i>), $^3J(F,P) = 9.1$ (<i>cis</i>)]; $\delta_H = 7.70$ – 7.50 (aromatic)
(CF ₃) ₃ Au(Opy) (7) ^[h]	-40.22	-26.19	6.8	$\delta_H = 8.60$ (m _c , 2H; H ^o), 8.03 (tt, 1H; H ^p), 7.75 (m _c , 2H; H ^m)
(CF ₃) ₃ Au(OPPh ₃) (8)	-37.57	-25.83	6.9	$\delta_P = 49.90$; $\delta_H = 7.75$ – 7.53 (aromatic)
(CF ₃) ₃ Au(tht) (9)	-33.26	-28.18	6.7	$\delta_H = 3.49$ (m _c , α -CH ₂), 2.18 (m _c , β -CH ₂)
(CF ₃) ₃ Au(SPPh ₃) (10)	-31.75	-29.17	7.2	$\delta_P = 47.13$; $\delta_H = 7.84$ – 7.57 (aromatic)

[a] Unless otherwise stated, all spectra were registered in CD₂Cl₂ solution at room temperature; chemical shifts (δ) are given in ppm relative to standard references (see Experimental) and coupling constants (J) in Hz; following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, spt = septet, tt = triplet of triplets, qspt = quartet of septets, m_c = multiplet centred at. [b] Signal corresponding to the mutually *trans*-standing CF₃ groups. [c] Signal corresponding to the CF₃ group *trans* to the L ligand. [d] Indicated is the coupling constant between chemically inequivalent CF₃ groups (*cis*). [e] Spectra registered in the slow ligand-exchange region (213 K). [f] The ¹H NMR spectrum of **4** was satisfactorily analyzed as a AA'MM'X system with the following homonuclear coupling constants: $^3J(H^o, H^m) = 5.6$, $^3J(H^m, H^p) = 7.8$, $^4J(H^o, H^p) = 1.5$, $^4J(H^o, H^o) = 0.5$, $^4J(H^m, H^m) = 1.5$, $^5J(H^o, H^m) = 0.8$. [g] The spectroscopic parameters of **5** are in keeping with previously reported data (see Refs. [26] and [33]). [h] The ¹H NMR spectrum of **7** was satisfactorily analyzed as a AA'MM'X system with the following homonuclear coupling constants: $^3J(H^o, H^m) = 6.6$, $^3J(H^m, H^p) = 7.8$, $^4J(H^o, H^p) = 1.1$, $^4J(H^o, H^o) = 2.1$, $^4J(H^m, H^m) = 2.1$, $^5J(H^o, H^m) = 0.7$.

Scheme 2. Replacement of the weakly coordinated Et₂O donor molecule in compound **1** by a range of monodentate neutral L and anionic X⁻ ligands. The cation is [PPh₄]⁺ where appropriate.

Synthesis and characterization of the neutral (CF₃)₃AuL derivatives: The labile character of the Et₂O ligand in the etherate **1** together with its reasonable thermal stability can be exploited for synthetic purposes. Thus, a number of neutral organogold(III) (CF₃)₃AuL derivatives (**2–10**) can be prepared by

replacement of the Et₂O molecule in the precursor species **1** by a series of representative L ligands (Scheme 2). It is interesting to note that similar attempts to prepare related silver complexes by replacement of the solvent donor ligands in (CF₃)₃Ag·solv (solv = dmso, MeCN, dmf, or other nitrogen bases) with soft donors such as PR₃ (R = Me, Ph, OMe) or AsF₃ failed.^[32] The phosphine derivative (CF₃)₃Au(PMe₃) (**5**) was already known: it was first prepared^[26] by complexation of naked (CF₃)₃Au with PMe₃ and later by treatment of (CF₃)₂AuI(PMe₃) with (CF₃)₂Cd·dme in the presence of excess CF₃I.^[33] Halide ligands X⁻ are also able to replace the labile Et₂O molecule in **1** furnishing the corresponding anionic [(CF₃)₃AuX]⁻ derivatives (Scheme 2) that we isolated recently (X = Cl, Br, I).^[24]

Monodentate L ligands were selected, covering a wide range of donor abilities with donor atoms including first- and second-row elements of the p-block, with the aim of exploring the stability of their corresponding complexes. All these compounds have been isolated and conveniently characterized by analytical and spectroscopic methods (see Experimental). The ¹H, ¹⁹F and ³¹P NMR spectroscopic parameters obtained from measurements in solution at room temperature are given in Table 1. Particularly valuable structural information in solution is derived from the ¹⁹F NMR spectra. The general spectral pattern

consists of two signals in 1:2 integrated ratio (typically a septet and a quartet), corresponding to the two types of chemically inequivalent CF_3 groups with no hint of fluxional exchange between them. Both sets of nuclei are mutually coupled with $^4J(\text{F},\text{F})$ values in the narrow 6.1–7.4 Hz range. Additional splitting of the signals is observed in the phosphine complexes **5** and **6**. In those compounds bearing typical π -acceptor ligands, namely $t\text{BuNC}$ (**2**), PMe_3 (**5**) and PPh_3 (**6**) the relative quartet vs. septet position appears inverted, a feature also observed in related isoelectronic Pt(II) derivatives.^[34]

The crystal and molecular structures of several representative examples have been experimentally established by single-crystal X-ray diffraction methods (Table 2). In the phosphine complexes $(\text{CF}_3)_3\text{Au}(\text{PMe}_3)$ (**5**; Figure 2a) and $(\text{CF}_3)_3\text{Au}(\text{PPh}_3)$ (**6**; Figure 2b), similar Au–P distances and virtually identical Au–C bond lengths are observed. The Au–P

bond in compound **6** (239.27(6) pm) is longer than in the homologous non-fluorinated compound $(\text{CH}_3)_3\text{Au}(\text{PPh}_3)$ (234.8(6) pm)^[35] or in the classic coordination compound $\text{Cl}_3\text{Au}(\text{PPh}_3)$ (232.9(2) pm).^[36] In the thioether complex $(\text{CF}_3)_3\text{Au}(\text{tth})$ (**9**), the structural features of the metal coordination environment (Figure 2c) compare well with those corresponding to the perfluorophenyl-derivative $(\text{C}_6\text{F}_5)_3\text{Au}(\text{tth})$.^[37] Again, the Au–S bond length in compound **9** (238.9(2) pm) is longer than in the classic coordination complex $\text{Cl}_3\text{Au}(\text{tth})$ (232.6(2) pm).^[38] In the pyridine complex $(\text{CF}_3)_3\text{Au}(\text{py})$ (**4**; Figure 3), the Au–N bond length (207.5(6) pm) is also substantially longer than in the Werner-type complex $\text{Cl}_3\text{Au}(\text{py})$ (199.3(7) pm).^[39] The elongated Au–L bonds found in these $(\text{CF}_3)_3\text{Au}\cdot\text{L}$ compounds ($\text{L} = \text{py}, \text{PPh}_3, \text{tth}$) in comparison with the corresponding chlorides $\text{Cl}_3\text{Au}\cdot\text{L}$, are clear evidence of the high *trans* influence of the CF_3 group.^[20]

Table 2. Relevant geometric parameters of the structurally characterized $(\text{CF}_3)_3\text{AuL}$ derivatives.^[a]

Compound	Au–C [pm] in $\text{CF}_3\text{–Au–CF}_3$ ^[b]	Au–C [pm] in E–Au–C	Au–E [pm]	$\text{CF}_3\text{–Au–CF}_3$ [°]	$\sum \angle$ ^[c] [°]
$(\text{CF}_3)_3\text{Au}(\text{CN}t\text{Bu})$ (2)	208.5(6)	205.8(5)	204.3(5)	179.7(2)	359.9
$(\text{CF}_3)_3\text{Au}(\text{py})$ (4)	207.4(9)	202.9(7)	207.5(6)	177.7(3)	360.1
$(\text{CF}_3)_3\text{Au}(\text{PMe}_3)$ (5) ^[d]	208.6(10)	208.3(10)	237.0(2)	174.5(4)	360.6
$(\text{CF}_3)_3\text{Au}(\text{PPh}_3)$ (6)	209.8(2)	209.0(3)	239.27(6)	175.2(1)	360.0
$(\text{CF}_3)_3\text{Au}(\text{Opy})$ (7) ^[e]	207.8(3)	202.5(3)	207.0(2)	178.2(1)	360.0
$(\text{CF}_3)_3\text{Au}(\text{OPPh}_3)$ (8) ^[f]	208.2(3)	200.1(3)	206.2(2)	176.9(1)	360.1
$(\text{CF}_3)_3\text{Au}(\text{tth})$ (9) ^[d]	208.8(8)	206.2(7)	238.9(2)	177.4(2)	360.1
$(\text{CF}_3)_3\text{Au}(\text{SPPPh}_3)$ (10) ^[g]	208.7(2)	205.3(2)	240.55(5)	179.4(1)	360.0

[a] A *trans* arrangement is meant in the indicated $\text{CF}_3\text{–Au–CF}_3$ and E–Au–C units with E denoting a chemical element. [b] Average of two independent values. [c] Summation of all adjacent E–Au–E' angles as a measure of planarity. [d] Average values for the two crystallographically independent molecules in the unit cell. [e] Au–O–N 119.26(15)°. [f] Au–O–P 131.10(11)°. [g] Au–S–P 105.90(3)°.

Figure 2. Displacement-ellipsoid diagram (50% probability) of the neutral $(\text{CF}_3)_3\text{AuL}$ derivatives with soft ligands: a) $(\text{CF}_3)_3\text{Au}(\text{PMe}_3)$ (**5**), b) $(\text{CF}_3)_3\text{Au}(\text{PPh}_3)$ (**6**), and c) $(\text{CF}_3)_3\text{Au}(\text{tth})$ (**9**).

Figure 3. Displacement-ellipsoid diagram (50% probability) of $(\text{CF}_3)_3\text{Au}(\text{py})$ (**4**). Only one set of the rotationally-disordered F atoms found in two of the CF_3 groups is shown.

Figure 4. Displacement-ellipsoid diagram (50% probability) of the following derivatives: a) $(\text{CF}_3)_3\text{Au}(\text{OPy})$ (**7**), b) $(\text{CF}_3)_3\text{Au}(\text{OPPh}_3)$ (**8**), and c) $(\text{CF}_3)_3\text{Au}(\text{SPhPh}_3)$ (**10**).

In compounds **5**, **6** and **9**, bearing soft PR_3 and SR_2 ligands (Figure 2), the Au–C bond lengths within each molecule are indistinguishable within the experimental error in spite of the lower *trans* influence associated with the PR_3 or SR_2 ligands vs. that assigned to the CF_3 group. Moreover, they do not significantly deviate from the Au–C bond length found in the homoleptic anionic derivative $[\text{NBu}_4][\text{Au}(\text{CF}_3)_4]$ (208.0(7) pm average).^[40] In complex **4**, however, the Au–C bond *trans* to the hard ligand pyridine is significantly shorter than those located *trans* to each other: 202.9(7) vs. 207.4(9) pm. A distinction in the Au–C distances involving chemically inequivalent CF_3 groups also becomes increasingly apparent in the phosphine sulphide complex **10** (205.3(2) vs. 208.7(2) pm), the pyridine *N*-oxide derivative **7** (202.5(3) vs. 207.8(3) pm), and in the phosphine oxide species **8** (200.1(3) vs. 208.2(3) pm), which respectively bear ligands with semipolar $\text{Ph}_3\text{P}^\oplus\text{--S}^\ominus$, $\text{py}^\oplus\text{--O}^\ominus$, and $\text{Ph}_3\text{P}^\oplus\text{--O}^\ominus$ bonds.^[41] In this set of compounds (Figure 4), the angles at the chalcogen atom, Au–E–N/P, gradually widen in the same sequence: Au–S–P 105.90(3)°, Au–O–N 119.26(15)°, and Au–O–P 131.10(11)°, a trend that can be probably related to the σ -donor ability of the ligand involved.^[42] The Au–S bond length in compound $(\text{CF}_3)_3\text{Au}(\text{SPhPh}_3)$ (240.55(5) pm) is similar to that found in the thioether derivative **9** (238.9(2) pm).

In $(\text{CF}_3)_3\text{Au}(\text{CNtBu})$ (**2**), the gold atom is surrounded by four C-donor ligands (Figure 5). The presence of a typical π -acceptor ligand, CNtBu, does not appear to have any significant effect on the Au– CF_3 bond length in *trans* position (Table 2). However, the Au–CNtBu bond distance (204.3(5) pm) is longer than that found in the homologous halo-derivative $\text{Br}_3\text{Au}(\text{CNtBu})$ (199(1) pm).^[43]

Figure 5. Displacement-ellipsoid diagram (50% probability) of $(\text{CF}_3)_3\text{Au}(\text{CNtBu})$ (**2**) with only one set of F atoms at half occupancy shown.

All the isolated $(\text{CF}_3)_3\text{AuL}$ compounds (**2–10**) show high thermal stability, as established by thermogravimetric and differential thermal analysis (TGA/DTA) of the corresponding solid samples (see Experimental). The results are given in the Supporting Information (Figures S14–S22). It is worth noting that the experimentally observed stability within the neutral $(\text{CF}_3)_3\text{AuL}$ series, as a function of the ancillary ligand L, is in reasonable agreement with that predicted by theoretical calculations (see below).

The small size of some of the $(\text{CF}_3)_3\text{AuL}$ molecules, together with the absence of significant intermolecular interactions in the solid, result in high volatility of the sample. Thus, the complexes

with MeCN (**3**), py (**4**), PMe₃ (**5**), and tht (**9**) boil between 205 and 223 °C at atmospheric pressure. Aside from the *t*BuNC complex **2**, which decomposes at 125 °C, all other compounds show high thermal stability with decomposition temperatures ranging from 220 to 302 °C. The upper value is set by the SPPH₃-derivative **10**, which is therefore the most stable species. It is worth noting that the pyridine-*N*-oxide complex **7** undergoes oxygen extrusion upon thermolysis giving rise to the pyridine complex **4**, as established by ¹⁹F NMR spectroscopy (Figure S23).

Lewis acidity of the (CF₃)₃Au fragment: In a previous work,^[24] we found that the unsaturated (CF₃)₃Au moiety is characterized by a marked stereochemical stability with clear preference for a T-shaped structure. This perfluorinated organogold(III) fragment is furthermore highly reluctant to undergo reductive elimination of CF₃–CF₃. Both these characteristic features can be considered as the main reasons underlying the intrinsic stability of the (CF₃)₃Au moiety. An analysis of the frontier orbitals of this d⁸ R₃M fragment reveals that the HOMO (Figure 6a) can be identified as a mainly Au–C bonding orbital involving the mutually *trans*-standing CF₃ groups. It is worth noting that this M–C bonding interaction is slightly antibonding for the C–F bonds, a feature connected with the negative fluorine hyperconjugation traditionally considered to operate in fluoroalkyl groups.^[44] The LUMO (Figure 6b) has a perpendicular arrangement and shows a highly directional empty orbital, which is responsible for the acidic properties of the unsaturated metal fragment. In this MO, antibonding interaction with filled F(p) orbitals is also observed to arise even with the empty metal-centered lobe, where an opposite stabilizing interaction might in turn be expected. This feature suggests that the empty coordination site has little affinity for the adjacent F substituents, as will be discussed below. We want now to focus on the Lewis acidity of the (CF₃)₃Au moiety, both in the absolute sense and in comparison with related species, such as the non-fluorinated homologous trimethylgold, (CH₃)₃Au, and the isoelectronic perfluoromethyl borane, (CF₃)₃B.

Figure 6. Frontier orbitals of the (CF₃)₃Au moiety: HOMO (a) and LUMO (b).

In the absence of a universal scale, the Lewis acidity of the (CF₃)₃Au fragment has been evaluated by three different criteria in use. The first one consists of a simple estimate of the LUMO energy.^[45] The LUMO of the (CF₃)₃Au unit in its ground state conformation is found to be located at considerably lower energy (–4.34 eV) than that of the non-fluorinated (CH₃)₃Au fragment

(–2.71 eV), which gives clear evidence of higher acidity in the former. Attending to this intrinsic criterion, the (CF₃)₃Au unit is also more acidic than the perfluorophenyl borane (C₆F₅)₃B, for which a LUMO energy of –3.93 eV has been calculated, but not as much as the perfluoromethyl borane (CF₃)₃B (–4.77 eV).^[45]

Another widely used criterion enabling measurement of the Lewis acidity of a chemical entity is given by the fluoride ion affinity (FIA). The absolute FIA values calculated for the T-shaped polytopes of the respective (CX₃)₃Au species using COF₂ as the reference fluoride carrier in the nearly isodesmic process indicated in Eq. (2) are as follows: 433 (X = F) vs. 298 (X = H) kJ mol^{–1}.

Figure 7. Lewis acidity scale in pF[–] values^[46] for selected neutral AX_n species. Only the highest acidity range is represented here.

Relying on this criterion, Christie and his coworkers have derived a quantitative scale of Lewis acidity conveniently using pF[–] values, which result from dividing the absolute fluoride affinities (in kcal mol^{–1} units) by 10.^[46] Relevant pF[–] values corresponding to the (CX₃)₃Au units (X = H, F) are shown in Figure 7 in graphical comparison with other neutral Lewis acids. By adhering to this quantitative scale, the Lewis acidity of the (CH₃)₃Au fragment (pF[–] = 7.1) coincides with that corresponding to SeF₄. It is clearly seen that the Lewis acidity of this organogold(III) fragment is substantially enhanced upon fluorination. Thus, the Lewis acidity of the perfluorinated (CF₃)₃Au moiety (pF[–] = 10.3) is higher than that assigned to BF₃ (pF[–] = 8.3) and comparable to those of (C₆F₅)₃B (pF[–] = 10.8) and AsF₅ (pF[–] = 10.6). Significantly stronger Lewis acids seem to be the neutral binary pentafluorides SbF₅ (pF[–] = 12.0) and especially AuF₅ in its monomeric (pF[–] = 14.1) or dimeric (pF[–] = 12.9) forms.^[47] The monomeric, square-pyramidal AuF₅ unit containing a highly oxidized gold(v) center (d⁶ electron configuration) has, in fact, been claimed to set the current upper limit of Lewis acidity for any neutral chemical species. Still stronger Lewis acids are to be found, however, in cationic species among which the F⁺ cation exhibits a pF[–] value as high as 36.1. It is worth noting that the (CF₃)₃Au unit is much weaker a Lewis acid than the superacidic isoelectronic borane (CF₃)₃B, for which a substantially higher FIA value of 556 kJ mol^{–1} (pF[–] = 13.3) has been calculated.^[15,45]

The close constitutional similarity of both $(\text{CX}_3)_3\text{Au}$ species ($\text{X} = \text{H}, \text{F}$) makes the comparison of their acidity by the referred theoretical criteria particularly relevant. Nevertheless, an experimental estimate of the Lewis acidity of the $(\text{CF}_3)_3\text{Au}$ fragment has also been carried out by the Gutmann–Beckett method.^[48] This method relies on the chemical shift variation, $\Delta\delta_{\text{P}}$, suffered by the Et_3PO base upon interaction with the acidic moiety (Lewis neutralization) and has been applied to acidic species of both metals and non-metals.^[49] The δ_{P} value of Et_3PO is shifted from 46.2 ppm in the free ligand to 79.6 ppm upon interaction with the $(\text{CF}_3)_3\text{Au}$ fragment, *i.e.*, $\Delta\delta_{\text{P}} = 33.4$ ppm. According to his value, the $(\text{CF}_3)_3\text{Au}$ unit can be ranked as a stronger Lewis acid than $(\text{C}_6\text{F}_5)_3\text{B}$, for which $\Delta\delta_{\text{P}} = 30.6$ ppm.^[49a, 49d] The same order is obtained attending to the intrinsic LUMO energies of $(\text{CF}_3)_3\text{Au}$ vs. $(\text{C}_6\text{F}_5)_3\text{B}$, as commented before. This order is, however, inverted when considering the FIA values just discussed. This inconsistency can be attributed to the B–F bond being much stronger than the Au–F one, namely 732 vs. 294.1 kJ mol^{-1} for the respective diatomic neutral fluorides.^[50] The large difference between B–F and Au–F bond strengths makes the FIA criterion particularly unfavorable for gold—a typical soft acid ('class *b*' metal) which prefers to bind larger and more polarizable ligands than fluoride.^[51]

Although the standard Gutmann–Beckett scale of Lewis acidity is set according to the δ_{P} shift of Et_3PO , consistent trends are generally obtained with Ph_3PO ($\delta_{\text{P}} = 25.1$ ppm).^[49a] In fact, if we compare the relative shift observed for the $(\text{CF}_3)_3\text{Au}(\text{OPPh}_3)$ complex ($\Delta\delta_{\text{P}}' = 24.8$ ppm; Table 1) with that reported for $(\text{C}_6\text{F}_5)_3\text{B}(\text{OPPh}_3)$ ($\Delta\delta_{\text{P}}' = 20.3$ ppm),^[49a–c] we again obtain an indication of higher acidity for the organogold(III) fragment. Using this secondary scale, it is interesting to note that the perfluoromethyl $(\text{CF}_3)_3\text{Au}$ unit is a stronger Lewis acid than the perfluorophenyl $(\text{C}_6\text{F}_5)_3\text{Au}$ moiety ($\Delta\delta_{\text{P}}' = 17.1$ ppm).^[31b]

Scheme 3. Fluorotropic processes in the unsaturated, isoleptic species $(\text{CF}_3)_3\text{B}$ (a)^[15] and $(\text{CF}_3)_3\text{Au}$ (b).

On the $[\text{Au}]\text{--CF}_3 \rightleftharpoons \text{F}[\text{Au}]\text{--CF}_2$ process: The main source of instability for the perfluoromethyl borane $(\text{CF}_3)_3\text{B}$ lies in the fact that the F substituents lie in close proximity to the superacidic boron center. The F^- ion is a hard base that forms particularly strong bonds with boron as commented above. A 1,2-F-shift is therefore energetically favored (-49.7 kJ mol^{-1}), whereby the saturated species $(\text{CF}_3)_2\text{B}(\text{CF}_2)\text{F}$ is formed (Scheme 3a). This fluorotropic process has been thoroughly studied by Willner and

his coworkers.^[15] We wanted now to explore the incidence that a similar process (Scheme 3b) might have in the chemistry of the isoleptic $(\text{CF}_3)_3\text{Au}$ fragment (hereafter labeled **A**).^[52,53]

When a fluorine atom of one of the mutually *trans*-standing CF_3 groups in **A** is forced to approach the metal center by varying the C–Au–F angle (α), the system energy rises steadily (Figure S1a) up to the point where the shifted F atom occupies the empty coordination site at $\alpha = 90^\circ$ (**B-cis**). Every stage in this endergonic *cis* 1,2-F-shift is metastable, including the highest point **B-cis** ($E = 81.4$ kJ mol^{-1} ; Figure 8)^[54] and all of them revert to the initial stage **A** in a spontaneous and barrierless way when the only restraint applied is removed (α set free). It is apposite to recall here that the LUMO of **A** (Figure 6b) shows antibonding interaction of the empty metal-centered lobe with filled p orbitals of the adjacent F atoms.

Figure 8. Energy scheme calculated for the $[\text{Au}]\text{--CF}_3 \rightleftharpoons \text{F}[\text{Au}]\text{--CF}_2$ fluorine shift (Scheme 3b) and subsequent CF_2 insertion into remaining $\text{Au}\text{--CF}_3$ bonds relative to the parent $(\text{CF}_3)_3\text{Au}$ species (**A**). Optimized stationary structures are depicted in Figure S3. An extended version of this energy scheme including higher-energy rotamers of the $[\text{Au}]\text{--C}_2\text{F}_5$ derivatives as well as other excited states is given in Figure S2.

A *trans* 1,2-F-shift in **A** gives an even higher and qualitatively different energy profile (Figure S1b). Here, the endpoint **B-trans** at $\alpha = 180^\circ$ is a high-energy local minimum (116.9 kJ mol^{-1} ; Figure 8) with a transition state being found at $\alpha = 72.3^\circ$ (333.6 kJ mol^{-1} ; Figure S1b). In the optimized geometry of **B-trans** (Figure S3), the planar CF_2 unit is placed exactly perpendicular to the metal coordination plane (dihedral angle: 90.0°). This arrangement is unsuited for any π M–C interaction to be established and accordingly, the $[\text{Au}]\text{--CF}_2$ interaction is depicted as a dative bond.

It is interesting to note that both stereoisomers (*cis* and *trans*) of **B** are standard square-planar, 16-electron species, but even so, they are less stable than the unsaturated, T-shaped, 14-electron moiety **A**. This destabilization upon 1,2-F-shift can be attributed to the unfavorable balance that results from the Au–F bond building at the expense of a C–F bond breaking. This is in sharp contrast with the boron case commented above, where the fluorotropic process $(\text{CF}_3)_3\text{B} \rightleftharpoons (\text{CF}_3)_2\text{B}(\text{CF}_2)\text{F}$ indeed gives a favorable balance to the saturated species on the right. In that case, the B–F bond energy overcomes the energy

expense derived from both the C–F bond breaking and the geometric rearrangement^[9] required to accommodate the initially triangular planar $(\text{CF}_3)_3\text{B}$ unit to the final tetrahedral shape in $(\text{CF}_3)_2\text{B}(\text{CF}_2)\text{F}$ (Scheme 3a). No such geometric rearrangement is needed in the gold $\mathbf{A} \rightleftharpoons \mathbf{B}$ system that relies on a basically square-planar frame (Scheme 3b).

Stereoisomer **B-*cis*** achieves substantial stabilization upon CF_2 insertion into any of the Au– CF_3 bonds giving rise to the again unsaturated species $\text{CF}_3\text{CF}_2\text{Au}(\text{CF}_3)\text{F}$ (**C**) in two of its isomeric forms (Figure 8). The relative orientation of the CF_2CF_3 group gives rise to different rotamers for each stereoisomer. As they do not differ much in energy from each other (Figure S2), only the most stable rotamer will be considered here. The stereoisomer that results from the CF_2 insertion in the *trans* Au– CF_3 bond is only marginally more stable (**C-2**: $-45.4 \text{ kJ mol}^{-1}$; Figure 8) than that resulting from the *cis* insertion (**C-3**: $-42.2 \text{ kJ mol}^{-1}$; Figure 8). A quite regular T-shaped structure is found in the optimized geometry of **C-3**, whereas an important Y-distortion is observed in stereoisomer **C-2** (Figure S3).

A similar insertion process in the **B-*trans*** species gives just a single stereoisomer, **C-0**, identified as a high-energy minimum in which the F ligand is located *trans* to the void (Figure S3). This particular arrangement is energetically unfavorable, and results in additional destabilization (**C-0**: $133.6 \text{ kJ mol}^{-1}$; Figure 8). It is worth noting that the high electronegativity of F favors a secondary Au⋯F bonding interaction with one of the β -F atoms (Figure S3). Moreover, if this interaction is forcibly removed, a new secondary interaction is spontaneously established, this time with an α -F atom of the CF_2CF_3 group. This new arrangement is even more destabilized (**C-0'**: $142.3 \text{ kJ mol}^{-1}$; Figure S2). No similar secondary interactions were observed in the stereoisomers **C-2** and **C-3**, in which the empty coordination site is *trans* to a perfluoroalkyl group (CF_2CF_3 and CF_3 , respectively). If such interactions are forcibly introduced, the system suffers destabilization (Figure S2) and reverts to the initial state when the restraints are removed. The difference in behavior between **C-0** and its stereoisomers **C-2** and **C-3** is clear evidence that fluoroalkyl ligands exert a much higher *trans* influence than fluoride. It would also be expected that the **C-0** species would transform into any of its more stable stereoisomers **C-2** and **C-3**.

From our current study, it becomes clear that the 1,2-F-shift is hindered as a potential decomposition path, thus adding to the stability of the $(\text{CF}_3)_3\text{Au}$ moiety (**A**). In fact, during our experimental work with this organogold(III) unit, we have found no evidence of formation of metal species containing the perfluoroethyl group $[\text{Au}]\text{--CF}_2\text{CF}_3$.

Ligand affinity of the $(\text{CF}_3)_3\text{Au}$ fragment: There is overwhelming evidence that trialkylgold(III) derivatives undergo reductive elimination *via* a dissociative mechanism as the initial step.^[55] A key point that determines the reaction progress in such R_3AuL systems should therefore be the ease of L dissociation. For this reason, we decided to calculate the affinity of the $(\text{CF}_3)_3\text{Au}$ fragment for a range of neutral ligands in order to evaluate their stability. These ligands include all those experimentally used in the synthesis of compounds $(\text{CF}_3)_3\text{AuL}$

(**1–10**) and are supplemented by a number of other donors selected for comparative purposes.

The molecular structures in the gas phase of all these compounds have been optimized by DFT calculations. The resulting minima are depicted in Figures S5–S13 and relevant geometric parameters are given in Table 3. In many instances, the obtained geometries can be directly compared with the corresponding solid-state structures experimentally established by single-crystal X-ray diffraction methods (Table 2). Excellent agreement is observed in the geometry of the $(\text{CF}_3)_3\text{Au}$ unit. However, the calculated Au–E distances are, in general, slightly longer than those experimentally observed. This means that the corresponding Au–E dissociation values, D_e , might be underestimated in our calculations. The order of calculated D_e values is graphically represented in Figure 9 and gives a ligand affinity scale of the $(\text{CF}_3)_3\text{Au}$ fragment.^[56]

The most stable compounds are clearly those formed with phosphines, the more basic PMe_3 providing even higher stability (**5**: $D_e 229 \text{ kJ mol}^{-1}$) than PPh_3 (**6**: $D_e 204 \text{ kJ mol}^{-1}$).

The stability of the compounds formed with semipolar pnictogen oxides, pyO (**7**: $D_e 151 \text{ kJ mol}^{-1}$) and Ph_3PO (**8**: $D_e 173 \text{ kJ mol}^{-1}$), is surpassed by that corresponding to the softer sulphide, Ph_3PS (**10**: $D_e 183 \text{ kJ mol}^{-1}$).

Figure 9. Affinity scale of the $(\text{CF}_3)_3\text{Au}$ fragment for various L ligands based on the dissociation energy (D_e) calculated for the corresponding $(\text{CF}_3)_3\text{Au}\text{--L}$ bond (Table 3). Considerably lesser stabilization is achieved by coordination to the non-fluorinated $(\text{CH}_3)_3\text{Au}$ fragment (right).

Table 3. Relevant geometric parameters of the indicated (CF₃)₃AuL compounds in the gas phase as optimized by DFT methods with indication of the Au–L dissociation energy (*D_e*).^[a–c]

Compound	<i>D_e</i> (Au–L) [kJ mol ^{–1}]	Au–E [pm]	Au–C [pm] in CX ₃ –Au–CX ₃ ^[d]	Au–C [pm] in E–Au–C	CX ₃ –Au–CX ₃ [°]
(CF ₃) ₃ Au ^[e]	–	–	209	207	172.9
(CF ₃) ₃ Au(OEt ₂) (1)	127	224	211	204.5	176.8
(CH ₃) ₃ Au(OEt ₂) (1H)	79	234	212	204	179.5
(CF ₃) ₃ AuCO	90	213	212	206.5	178.5
(CF ₃) ₃ Au(CN <i>t</i> Bu) (2)	178	209	211.5	206.5	178.2
(CF ₃) ₃ Au(Si <i>Nt</i> Bu) ^[f]	139	228 ^[g]	212	207	179.8
(CF ₃) ₃ Au(NCMe) (3)	122	215	211	204	177.6
(CF ₃) ₃ Au(py) (4)	169	216	211	205	176.9
(CF ₃) ₃ Au(PCMe) ^[h]	106	249 ^[i]	212	208	179.3
(CF ₃) ₃ Au(PC ₅ H ₅)	152	248	212	208	179.7
(CF ₃) ₃ Au(PMe ₃) (5)	229	245.5	211	209.5	174.4
(CH ₃) ₃ Au(PMe ₃) (5H)	160	241	213.5	208	175.1
(CF ₃) ₃ Au(PPh ₃) (6)	204	248	212	210	173.1
(CF ₃) ₃ Au(PF ₃)	90	245.5	211.5	207.5	176.0
(CF ₃) ₃ Au(OPy) (7) ^[j]	151	217	211	204.5	176.7
(CF ₃) ₃ Au(OPPh ₃) (8) ^[k]	173	215	211	204	176.4
(CF ₃) ₃ Au(SEt ₂)	166	251.5	211.5	208	178.6
(CF ₃) ₃ Au(tht) (9)	149	252	211.5	207.5	178.7
(CF ₃) ₃ Au(SPPPh ₃) (10) ^[l]	183	251.5	211.5	208	178.2

[a] The naked (CF₃)₃Au fragment (L = nil) as well as ether and phosphine complexes of the non-fluorinated (CH₃)₃Au fragment (**1H** and **5H**; values in italics) are also included for comparison. [b] A *trans* arrangement is meant in the indicated CX₃–Au–CX₃ (X = H, F) and E–Au–C units with E denoting a chemical element. [c] Atomic coordinates of the optimized structures are given in the Supporting Information. [d] Average value. [e] Ref. [24]. [f] The Si*Nt*Bu unit shows an asymmetric side-on coordination favoring the Au–N interaction. [g] Indicated is the Au–N distance, the Au–Si separation being 282 pm. [h] The PCMe unit is π-coordinated to the metal center. [i] Distance from the metal to the centroid of the π-coordinated ligand. [j] Au–O–N 118.6°. [k] Au–O–P 125.9°. [l] Au–S–P 100.7°.

Intermediate stabilization is attained with py (**4**: *D_e* 169 kJ mol^{–1}) and *t*BuNC (**2**: *D_e* 178 kJ mol^{–1}). Less stable, however, are the complexes formed with the heavier-element homologues, PC₅H₅ (*D_e* 152 kJ mol^{–1}) and *t*BuNSi (*D_e* 139 kJ mol^{–1}). In the (CF₃)₃Au(Si*Nt*Bu) complex (Figure S6), the silylated ligand is coordinated in a highly asymmetric way, clearly slipped towards the N atom. In the optimized geometry of the phosphabenzene complex, (CF₃)₃Au(PC₅H₅) (Figure S8), little modification is observed in the heteroaromatic ring with respect to the free ligand,^[57] in keeping with other structurally characterized metal complexes.^[58] Thus, a planar geometry is found at the P atom

with a low C–P–C angle (105°) and indistinguishable C–C bond distances within the ring (139 pm av.) consistent with a delocalized aromatic conditon. The Au–P distance (248 pm) is, however, appreciably longer than those found in linear gold(I) complexes of various substituted λ³-phosphinine monodentate ligands: ClAu(PC₅H₂*t*Bu₃-2,4,6) (221.9(2) pm),^[59] ClAu(PC₅H₂Ph₂-2,6-Me-4) (220.62(7) pm, av.),^[60] ClAu(PC₅H₂R₂-2,6-Ph-4) (223.4(3) pm for R = Me; ca. 222 pm for R = Ph),^[61] ClAu(PC₅H₂R-2-Ph₂-4,6) (220.8(1) pm, av.; R = C₆H₃(OMe)₂-3,4),^[62] ClAu{PC₅HR-2-Me-3-Ph₂-4,6} (220.40(7) pm; R = C₆H₃Me₂-2,3),^[63] ClAu{PC₅H₃(SiMe₃)₂-2,6} (221.1(2)

pm) and $[\text{Au}(\text{PC}_5\text{H}_5(\text{SiMe}_2\text{R})_2)_2][\text{GaCl}_4]$ (228.2(4) pm, av. for $\text{R} = \text{Me}$; 226.3(2) pm, av. for $\text{R} = \text{CCPh}$).^[64] The most salient difference with the homologous py complex **4** is the relative disposition of the heteroaromatic EC_5H_5 ring with respect to the metal coordination plane, the dihedral angle being much smaller for $\text{E} = \text{P}$ (20.3°) than for $\text{E} = \text{N}$ (81.2°). It is worth noting that the latter is in excellent agreement with that experimentally determined for complex **4** (78.2°). The lesser stability of $(\text{CF}_3)_3\text{Au}(\text{PC}_5\text{H}_5)$ in comparison with $(\text{CF}_3)_3\text{Au}(\text{NC}_5\text{H}_5)$ can be attributed to the phosphabenzene ligand being a weaker σ donor and better π -acceptor than py.^[65]

Just moderately stable compounds are those formed with the hard ligands Et_2O (**1**) and MeCN (**3**), for which $D_e \sim 125 \text{ kJ mol}^{-1}$. These Lewis bases are well known as typical weakly coordinating ligands.^[66] Considering the modest D_e value required to set free the unsaturated metal fragment, these solvates are indeed suitable synthons for the naked $(\text{CF}_3)_3\text{Au}$ unit. Substantially more stabilized are complexes with soft thioether ligands, such as open-chain Et_2S (D_e 166 kJ mol^{-1}) or alicyclic tht (**9**: D_e 149 kJ mol^{-1}). In contrast, the complex formed with the heavier-element homologue of acetonitrile, $\text{MeC}\equiv\text{P}$, is significantly less stable (D_e 106 kJ mol^{-1}). Both $(\text{CF}_3)_3\text{Au}(\text{ECMe})$ complexes, however, show quite different structural patterns. Thus, side-on coordination is more stable for the heavier $\text{MeC}\equiv\text{P}$ ligand (Figure S7), whereas the standard end-on coordination is found for $\text{MeC}\equiv\text{N}$. Although sought by different approaches, no minimum was found for side-on coordination in the latter case. Side-on coordination of the phosphalkyne ligand was experimentally found in the cationic gold(I) complex $[(\text{RfBu}_2\text{P})\text{Au}(\eta^2\text{-P}\equiv\text{CtBu})][\text{SbF}_6]$ ($\text{R} = \text{C}_6\text{H}_4\text{Ph-2}$).^[67]

Identical stabilization is attained with the prototypical π -acceptor ligands CO and PF_3 : D_e 90 kJ mol^{-1} . These compounds are the least stable within the whole set under study. As in the phosphabenzene case, the poor σ -donor ability of the CO and PF_3 ligands results in weaker $[\text{Au}]\text{-L}$ σ bonds. Moreover, there is little chance for the $(\text{CF}_3)_3\text{Au}$ unit to supply any significant π back-bonding contribution that might strengthen the $[\text{Au}]\text{-L}$ bond by synergy. In fact, we were unable to prepare the carbonyl derivative $(\text{CF}_3)_3\text{AuCO}$ by replacement of the labile Et_2O molecule in compound **1**, at least under the experimental conditions that proved successful in every other case (Scheme 2).

Within the set of L bases chosen for the current study, the P-donor ligands prove to be particularly versatile, as they encompass the whole stability range (Figure 9). Thus, the upper limit is set by the highly basic phosphine PMe_3 , whereas the lower limit is set by the poor donor PF_3 . In between are found unsaturated P-donor ligands, as phosphabenzene, PC_5H_5 , or the phosphalkyne $\text{MeC}\equiv\text{P}$.

We finally wanted to compare the stabilization achieved by coordination of a given ligand L to the $(\text{CF}_3)_3\text{Au}$ species with that attained with the non-fluorinated $(\text{CH}_3)_3\text{Au}$ fragment. For this purpose, we selected compounds $(\text{CH}_3)_3\text{Au}(\text{OEt}_2)$ (**1H**) and $(\text{CH}_3)_3\text{Au}(\text{PMe}_3)$ (**5H**) as representative examples of complexes with weakly and strongly coordinated ligands. It was found that, in both cases, coordination to the $(\text{CH}_3)_3\text{Au}$ fragment provides substantially less stabilization (Table 3; Figure 9). By comparing the optimized geometries of the $(\text{CX}_3)_3\text{Au}(\text{OEt}_2)$ molecules ($\text{X} = \text{H}, \text{F}$; Figure S5), it is worth noting that the oxygen atom in the fluorinated derivative **1** undergoes little pyramidalization, with the sum of subtended bond angles (352°) being appreciably greater

than in the non-fluorinated counterpart **1H** (341°). This is probably an additional effect of the stronger acidity of the $(\text{CF}_3)_3\text{Au}$ moiety that should induce higher polarization of the electron density at the donor atom. From the experimental point of view and as commented above, compound **1** can be handled in solution at room temperature without noticeable decomposition, whereas **1H** begins to decompose already at -40°C .^[27] In a similar way, $(\text{CF}_3)_3\text{Au}(\text{PPh}_3)$ (**6**) is stable up to 251°C , whereas its non-fluorinated homologue $(\text{CH}_3)_3\text{Au}(\text{PPh}_3)$ decomposes at 120°C .^[68] Thus, fluorination of the trimethylgold moiety, $(\text{CH}_3)_3\text{Au}$, results in substantial stability enhancement in the corresponding $(\text{CF}_3)_3\text{AuL}$ derivatives, as shown experimentally and confirmed by theoretical calculations.

Conclusions

The perfluorinated $(\text{CF}_3)_3\text{Au}$ moiety is presented here as a highly acidic organogold(III) fragment. As established by theoretical and experimental methods, its Lewis acidity largely exceeds that corresponding to the non-fluorinated homologous species $(\text{CH}_3)_3\text{Au}$, closely approaching that of the familiar $(\text{C}_6\text{F}_5)_3\text{B}$ derivative. This result reinforces the idea of the CF_3 group acting as an efficient electron-withdrawing ligand with high group electronegativity.^[18] Since CF_3 is the organic group with the highest fluorine content per carbon atom, the $(\text{CF}_3)_3\text{Au}$ moiety possibly excels as the strongest Lewis acid of any conceivable R_3Au organogold species.

The neutral etherate $(\text{CF}_3)_3\text{Au}\cdot\text{OEt}_2$ (**1**) provides a convenient experimental entry to the chemistry of the perfluorinated $(\text{CF}_3)_3\text{Au}$ moiety, which is currently underdeveloped. The modest bond dissociation energy of the coordinated Et_2O ligand together with its high lability make compound **1** a useful synthon of the unsaturated $(\text{CF}_3)_3\text{Au}$ fragment. In fact, a range of neutral $(\text{CF}_3)_3\text{AuL}$ compounds (**2–10**) have been synthesized therefrom (Scheme 2). The L ligands, which include a variety of C-, N-, P-, O- and S-donors, have been selected to cover a wide range of donor abilities. Compounds **3–10** exhibit marked thermal stability, as they decompose at temperatures $>200^\circ\text{C}$. It is worth noting that the stability of the saturated $(\text{CF}_3)_3\text{AuL}$ compounds largely exceeds that of the non-fluorinated $(\text{CH}_3)_3\text{AuL}$ homologues in the few cases where such comparison can be experimentally established. The stabilization enhancement by fluorination has been estimated to amount to 50–70 kJ mol^{-1} (Table 3; Figure 9). This remarkable stability makes the $(\text{CF}_3)_3\text{Au}$ moiety especially appealing for synthetic and applied purposes. For this reason, a ligand affinity scale has been elaborated by DFT methods (Figure 9) that might provide a functional guide for reactivity studies. Given the stereochemical stability of the T-shaped $(\text{CF}_3)_3\text{Au}$ moiety, little deformation energy is required to accommodate the metal coordination sphere for the incoming L ligand.^[16,69] For this reason, our estimates of ligand dissociation energies in the series of $(\text{CF}_3)_3\text{AuL}$ complexes provide a reliable measure of the actual Au-L interaction energy.

It is also worth noting, that the high energy-profile calculated for the $[\text{Au}]\text{-CF}_3 \rightleftharpoons \text{F-}[\text{Au}]\text{-CF}_2$ fluorine shift (Scheme 3b) makes this process less important as a potential decomposition channel, thus contributing further as an additional source of stability.

In summary, fluorination of the trimethylgold moiety, $(\text{CH}_3)_3\text{Au}$, raises the Lewis acidity of the Au center in $(\text{CF}_3)_3\text{Au}$ close to that of $(\text{C}_6\text{F}_5)_3\text{B}$ and results also in substantial stability enhancement in the corresponding $(\text{CF}_3)_3\text{AuL}$ complexes. These advantageous features together with its marked stereochemical stability and its reluctance to undergo diverting side-reactions, such as fluorotropism or reductive elimination,^[24] make the single-site $(\text{CF}_3)_3\text{Au}$ fragment appealing for reactivity and mechanistic studies. Considering also the current interest in the involvement of organogold(III) complexes in synthetic and catalytic processes,^[70] it might be anticipated that the $(\text{CF}_3)_3\text{Au}$ system may find interesting applications, as it unites the reactivity potential of organogold complexes with the performance of the highly acidic $(\text{C}_6\text{F}_5)_3\text{B}$ species.

Experimental Section

General Procedures and Materials. Unless otherwise stated, the reactions and manipulations were carried out under purified argon using Schlenk techniques. Solvents were dried using an MBraun SPS-800 System. The parent species $[\text{PPh}_4][(\text{CF}_3)_3\text{AuI}]$ was obtained as described elsewhere.^[24] Other chemicals were purchased from standard commercial suppliers and used as received. Elemental analyses were carried out using a Perkin Elmer 2400 CHNS/O Series II microanalyzer. IR spectra were recorded on neat solid samples using a Perkin-Elmer Spectrum FT-IR spectrometer ($4000\text{--}250\text{ cm}^{-1}$) equipped with an ATR device. Mass spectra (MS) were registered on Bruker MicroFlex or AutoFlex spectrometers. No clear peaks were detected, however, for any of the neutral species $(\text{CF}_3)_3\text{AuL}$ (**2–10**) by using either positive or negative MALDI-TOF techniques. NMR spectra were recorded on any of the following Bruker spectrometers: ARX 300 or AV 400. Unless otherwise stated, the spectroscopic measurements were carried out at room temperature. Chemical shifts of the measured nuclei (δ in ppm) are given with respect to the standard references in use: SiMe_4 (^1H and ^{13}C) and CFCl_3 (^{19}F) and 85% aqueous H_3PO_4 (^{31}P). Experimentally obtained NMR spectroscopic parameters are given in Table 1 and are therefore omitted in the corresponding synthetic entry. Thermogravimetric and differential thermal analyses (TGA/DTA) were performed using a SDT 2960 instrument at heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under N_2 atmosphere. Melting points were taken at the maximum of the DTA peak and verified by visual inspection of samples placed on glass plates using an Olympus BH-2 microscope fitted with a Linkam TMS-91 temperature controller with hot stage.

Safety note: Although we have not encountered any problems working under the conditions detailed below (synthesis of **1**), perchlorate salts are potentially explosive when in contact with organic solvents and ligands. For this reason, only small amounts of these materials should be prepared and they should always be handled with great caution.^[71]

Synthesis of $(\text{CF}_3)_3\text{Au}\cdot\text{OEt}_2$ (1**):** Addition of the equimolar amount of AgClO_4 (24 mg, 0.11 mmol) to a solution of $[\text{PPh}_4][(\text{CF}_3)_3\text{AuI}]$ (0.10 g, 0.11 mmol) in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ (2 and 10 cm^3 , respectively) in the dark caused the immediate precipitation of AgI. After 30 min of stirring, the solvent mixture was replaced by another one consisting of $\text{Et}_2\text{O}/n$ -hexane (5 and 15 cm^3 , respectively), and the resulting suspension was allowed to stand at $-80\text{ }^\circ\text{C}$ overnight. Filtering the solid off, a solution of the etherate **1** was obtained, which is suitable for most synthetic purposes (80% yield estimated on further reactions). By evaporation of this solution to dryness at $0\text{ }^\circ\text{C}$, a white residue appeared, which was redissolved in n -hexane. By keeping this extract at $-80\text{ }^\circ\text{C}$ for 2 days, a deliquescent white solid was obtained still containing some free Et_2O (Figure 1).

Synthesis of $(\text{CF}_3)_3\text{Au}(\text{CNtBu})$ (2**):** To a solution of compound **1** (92 μmol) in $\text{Et}_2\text{O}/n$ -hexane (5 and 15 cm^3 , respectively) prepared as just described, $t\text{BuNC}$ (11 mm^3 , 92 μmol) was added, and the resulting mixture was stirred for 30 min. The removal of the solvent by vacuum evaporation afforded a white solid, which was suspended in n -hexane (3 cm^3), filtered, dried and identified as compound **2** (28 mg, 58 μmol , 63% yield). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.577 MHz, CD_2Cl_2): $\delta_{\text{C}} = 29.4\text{ ppm}$ (s; CH_3). IR (cm^{-1}): 2997 (w), 2283 (m, $\text{C}\equiv\text{N}$), 1617 (w), 1477 (w), 1456 (w), 1437 (w), 1379 (m), 1259 (w), 1236 (w), 1160 (m), 1131 (s), 1100 (s), 1073 (vs), 1038 (vs), 954 (m), 934 (m), 831 (m), 802 (m), 751 (w), 728 (s), 714 (s), 689 (m), 639 (w), 527 (s), 451 (w), 399 (w), 339 (w), 329 (w), 307 (w), 294 (s), 278 (m), 263 (m). Anal. Calcd (%) for $\text{C}_8\text{H}_9\text{AuF}_9\text{N}$: C, 19.73; H, 1.86; N, 2.88. Found: C, 20.22; H, 1.68; N, 2.84. Single crystals suitable for X-ray diffraction purposes were obtained by slow evaporation of a $\text{Et}_2\text{O}/n$ -hexane solution (1 and 2 cm^3 , respectively) of 7 mg of compound **2** at room temperature.

Synthesis of $(\text{CF}_3)_3\text{Au}(\text{NCMe})$ (3**):** Using the procedure just described for synthesizing **2**, compound **3** was prepared starting from an $\text{Et}_2\text{O}/n$ -hexane solution of compound **1** (92 μmol) and MeCN (4.8 mm^3 , 92 μmol). Complex **3** was obtained as a white solid (28 mg, 62 μmol , 68% yield); m.p. $96\text{ }^\circ\text{C}$; b.p. $209\text{ }^\circ\text{C}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.577 MHz, CD_2Cl_2): $\delta_{\text{C}} = 120.5$ (s; $\text{C}\equiv\text{N}$), 3.6 ppm (s; CH_3). IR (cm^{-1}): 2959 (m), 2901 (w), 2346 (m; ν_2 : $\text{C}\equiv\text{N}$), 2316 (m; $\nu_3+\nu_4$),^[72] 1408 (w), 1370 (w), 1260 (m), 1170 (s), 1139 (s), 1095 (s), 1040 (vs), 1025 (vs), 955 (s), 866 (m), 799 (s), 736 (s), 716 (m), 534 (w), 460 (w), 402 (m), 321 (s), 307 (s), 266 (s). Anal. Calcd (%) for $\text{C}_5\text{H}_3\text{AuF}_9\text{N}$: C, 13.49; H, 0.68; N, 3.15. Found: C, 13.31; H, 0.72; N, 3.33.

Synthesis of $(\text{CF}_3)_3\text{Au}(\text{py})$ (4**):** Using the procedure just described for synthesizing **2**, compound **4** was prepared starting from an $\text{Et}_2\text{O}/n$ -hexane solution of compound **1** (92 μmol) and py (7.4 mm^3 , 92 μmol). Complex **4** was obtained as a white solid (29 mg, 60 μmol , 65% yield); m.p. $177\text{ }^\circ\text{C}$; b.p. $223\text{ }^\circ\text{C}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.577 MHz, CD_2Cl_2): $\delta = 149.6$ (s; C^{O}), 142.4 (s; C^{P}), 127.8 ppm (s; C^{m}). IR (cm^{-1}): 3128 (w), 1617 (m), 1493 (w), 1460 (s), 1436 (w), 1260 (m), 1166 (s), 1126 (s), 1112 (s), 1080 (vs), 1044 (vs), 1034 (vs), 1020 (vs), 1009 (vs), 980 (s), 948 (s), 871 (w), 799 (m), 759 (s), 731 (m), 715 (m), 688 (vs), 656 (m), 526 (m), 446 (w), 432 (w), 395 (w), 341 (w), 313 (m), 303 (s), 280 (w), 262 (m). Anal. Calcd (%) for $\text{C}_8\text{H}_5\text{AuF}_9\text{N}$: C, 19.89; H, 1.04; N, 2.90. Found: C, 19.91; H, 1.02; N, 3.08. Single crystals suitable for X-ray diffraction purposes were obtained by slow evaporation of a $\text{Et}_2\text{O}/n$ -hexane solution (1 and 2 cm^3 , respectively) of 7 mg of compound **4** at room temperature.

Synthesis of $(\text{CF}_3)_3\text{Au}(\text{PMe}_3)$ (5**):** Using the procedure just described for synthesizing **2**, compound **5** was prepared starting from an $\text{Et}_2\text{O}/n$ -hexane solution of compound **1** (92 μmol) and a 1 M solution of PMe_3 in toluene (92 mm^3 , 92 μmol). Complex **5**, which had already been prepared by other methods,^[26,33] was obtained as a white solid (24 mg, 50 μmol , 54% yield); m.p. $151\text{ }^\circ\text{C}$; b.p. $214\text{ }^\circ\text{C}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.577 MHz, CD_2Cl_2): $\delta = 14.7\text{ ppm}$ (d, $^1J(^{13}\text{C}, ^{31}\text{P}) = 36.0\text{ Hz}$; CH_3). IR (cm^{-1}): 2936 (w), 1436 (w), 1426 (w), 1322 (w), 1302 (m), 1158 (s), 1104 (s), 1058 (vs), 1038 (vs), 1016 (vs), 958 (vs), 867 (s), 764 (m), 750 (m), 719 (m), 713 (m), 681 (w), 525 (w), 366 (w), 298 (m), 278 (m). Anal. Calcd (%) for $\text{C}_6\text{H}_9\text{AuF}_9\text{P}$: C, 15.01; H, 1.89. Found: C, 15.09; H, 1.69. Single crystals suitable for X-ray diffraction purposes were obtained by slow evaporation of a $\text{Et}_2\text{O}/n$ -hexane solution (1 and 2 cm^3 , respectively) of 7 mg of compound **5** at room temperature.

Synthesis of $(\text{CF}_3)_3\text{Au}(\text{PPh}_3)$ (6**):** Using the procedure just described for synthesizing **2**, compound **6** was prepared starting from an $\text{Et}_2\text{O}/n$ -hexane solution of compound **1** (92 μmol) and PPh_3 (24 mg, 92 μmol). Complex **6** was obtained as a white solid (34 mg, 51 μmol , 56% yield); m.p. $153\text{ }^\circ\text{C}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.577 MHz, CD_2Cl_2): $\delta = 134.4$ (d, $^2J(^{13}\text{C}, ^{31}\text{P}) = 11.1\text{ Hz}$; C^{O}), 133.0 (d, $^4J(^{13}\text{C}, ^{31}\text{P}) = 3.0\text{ Hz}$; C^{P}), 129.7 (d, $^3J(^{13}\text{C}, ^{31}\text{P}) = 11.9\text{ Hz}$; C^{m}), 126.6 ppm (d, $^1J(^{13}\text{C}, ^{31}\text{P}) = 58.8\text{ Hz}$; C^{iso}). IR (cm^{-1}): 3060 (w), 1587 (w), 1484 (m), 1439 (m), 1334 (w), 1316 (w), 1190 (w), 1150 (s), 1124 (s), 1099 (vs), 1049 (vs), 1033 (vs), 997 (s), 975 (m),

933 (w), 924 (w), 844 (w), 757 (m), 745 (s), 721 (m), 707 (s), 691 (vs), 617 (w), 527 (vs), 511 (s), 495 (s), 458 (m), 446 (w), 423 (m), 406 (w), 396 (w), 374 (w), 334 (w), 290 (s), 276 (w), 269 (w). Anal. Calcd (%) for $C_{21}H_{15}AuF_9P$: C, 37.86; H, 2.27. Found: C, 37.65; H, 2.09. Single crystals suitable for X-ray diffraction purposes were obtained by slow evaporation of a Et_2O/n -hexane solution (1 and 2 cm^3 , respectively) of 7 mg of compound **6** at room temperature.

Synthesis of $(CF_3)_3Au(Opy)$ (7): By using the procedure just described for synthesizing **2**, compound **7** was prepared starting from an Et_2O/n -hexane solution of compound **1** (92 μ mol) and Opy (8.7 mg, 92 μ mol). Complex **7** was obtained as a white solid (20 mg, 40 μ mol, 44% yield); m.p. 108 $^{\circ}C$. $^{13}C\{^1H\}$ NMR (100.577 MHz, CD_2Cl_2): δ = 141.2 (s; C^O), 137.9 (s; C^P), 128.0 ppm (s; C^m). IR (cm^{-1}): 3127 (w), 3103 (w), 1620 (w), 1479 (s), 1436 (w), 1253 (w), 1210 (m), 1163 (m), 1147 (s), 1098 (s), 1065 (vs), 1055 (vs), 1034 (vs), 1021 (vs), 932 (m), 832 (s), 810 (m), 772 (s), 734 (m), 713 (m), 689 (w), 669 (s), 643 (w), 585 (s), 556 (w), 528 (m), 473 (s), 353 (s), 306 (s), 280 (w), 264 (s). Anal. Calcd (%) for $C_8H_5AuF_9NO$: C, 19.25; H, 1.01; N, 2.81. Found: C, 19.42; H, 0.90; N, 3.02. Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a layer of n -hexane (10 cm^3) into a solution of compound **7** (7 mg) in Et_2O (3 cm^3) at 4 $^{\circ}C$.

Synthesis of $(CF_3)_3Au(OPPh_3)$ (8): Using the procedure just described for synthesizing **2**, compound **8** was prepared starting from an Et_2O/n -hexane solution of compound **1** (92 μ mol) and $OPPh_3$ (26 mg, 92 μ mol). Complex **8** was obtained as a white solid (38 mg, 56 μ mol, 61%); m.p. 145 $^{\circ}C$. $^{13}C\{^1H\}$ NMR (100.577 MHz, CD_2Cl_2): δ = 134.2 (d, $^4J(^{13}C, ^{31}P)$ = 2.8 Hz; C^P), 133.0 (d, $^2J(^{13}C, ^{31}P)$ = 11.1 Hz; C^O), 129.5 (d, $^3J(^{13}C, ^{31}P)$ = 13.1 Hz; C^m), 127.8 ppm (d, $^1J(^{13}C, ^{31}P)$ = 108.9 Hz; C^{iso}). IR (cm^{-1}): 3070 (w), 1590 (w), 1485 (w), 1440 (m), 1315 (w), 1180 (m), 1163 (w), 1147 (m), 1115 (vs; O=P), 1101 (s), 1084 (vs), 1050 (vs), 1038 (vs), 1022 (vs), 996 (vs), 985 (s), 937 (m), 851 (w), 754 (m), 746 (m), 727 (vs), 692 (s), 617 (w), 552 (s), 531 (vs), 481 (m), 442 (m), 431 (m), 400 (w), 389 (w), 352 (m), 318 (m), 309 (m), 294 (w), 281 (w), 265 (m). Anal. Calcd (%) for $C_{21}H_{15}AuF_9OP$: C, 36.97; H, 2.22. Found: C, 36.83; H, 2.11. Single crystals suitable for X-ray diffraction purposes were obtained by slow evaporation of a Et_2O/n -hexane solution (1 and 2 cm^3 , respectively) of 7 mg of compound **8** at room temperature.

Synthesis of $(CF_3)_3Au(tht)$ (9): Using the procedure just described for synthesizing **2**, compound **9** was prepared starting from an Et_2O/n -hexane solution of compound **1** (92 μ mol) and THT (8.2 mm³, 92 μ mol). Complex **9** was obtained as a white solid (17 mg, 35 μ mol, 38% yield); m.p. 89 $^{\circ}C$; b.p. 205 $^{\circ}C$. $^{13}C\{^1H\}$ NMR (100.577 MHz, CD_2Cl_2): δ = 40.0 (s; α -CH₂), 30.2 ppm (s; β -CH₂). IR (cm^{-1}): 2941 (w), 2873 (w), 1447 (w), 1438 (w), 1314 (w), 1278 (w), 1263 (w), 1213 (w), 1156 (s), 1127 (w), 1104 (vs), 1038 (vs), 961 (s), 896 (m), 807 (m), 730 (m), 713 (m), 666 (w), 653 (m), 528 (w), 516 (w), 477 (w), 310 (m), 295 (m), 277 (w), 266 (w). Anal. Calcd (%) for $C_7H_5AuF_9S$: C, 17.08; H, 1.64; S, 6.52. Found: C, 17.07; H, 1.49; S, 6.72. Single crystals suitable for X-ray diffraction purposes were obtained by slow evaporation of a Et_2O/n -hexane solution (1 and 2 cm^3 , respectively) of 7 mg of compound **9** at room temperature.

Synthesis of $(CF_3)_3Au(SPPH_3)$ (10): Using the procedure just described for synthesizing **2**, compound **10** was prepared starting from an Et_2O/n -hexane solution of compound **1** (92 μ mol) and $SPPH_3$ (27 mg, 92 μ mol). Complex **10** was obtained as a white solid (39 mg, 56 μ mol, 61% yield); m.p. 192 $^{\circ}C$. $^{13}C\{^1H\}$ NMR (100.577 MHz, CD_2Cl_2): δ = 134.5 (d, $^4J(^{13}C, ^{31}P)$ = 2.9 Hz; C^P), 133.6 (d, $^2J(^{13}C, ^{31}P)$ = 11.2 Hz; C^O), 130.0 (d, $^3J(^{13}C, ^{31}P)$ = 13.4 Hz; C^m), 126.3 ppm (d, $^1J(^{13}C, ^{31}P)$ = 86.6 Hz; C^{iso}). IR (cm^{-1}): 3083 (w), 1588 (w), 1482 (w), 1439 (m), 1335 (w), 1314 (w), 1187 (w), 1150 (s), 1118 (s), 1104 (vs), 1094 (vs), 1054 (vs), 1042 (vs), 996 (s), 982 (m), 973 (m), 935 (m), 854 (w), 842 (w), 758 (m), 747 (m), 718 (s), 699 (s), 686 (s), 638 (w), 618 (m), 585 (vs; S=P), 538 (w), 517 (vs), 504 (vs), 473 (m), 447 (m), 434 (m), 403 (w), 394 (w), 352 (m), 317 (m), 290 (m), 265 (m). Anal. Calcd (%) for $C_{21}H_{15}AuF_9PS$: C, 36.12; H, 2.17; S, 4.59. Found: C, 36.56; H, 2.11; S, 4.75. Single crystals suitable for X-ray

diffraction purposes were obtained by slow evaporation of a Et_2O/n -hexane solution (1 and 2 cm^3 , respectively) of 7 mg of compound **10** at room temperature.

Synthesis of $[PPh_4][(CF_3)_3AuCl]$: To a solution of compound **1** (92 μ mol) in Et_2O/n -hexane (5 and 15 cm^3 , respectively) prepared as described above was added $[PPh_4]Cl$ (34 mg, 92 μ mol). The resulting mixture was stirred for 30 min. and then concentrated to dryness. Treatment of the resulting residue with $iPrOH$ (3 cm^3) at $-30^{\circ}C$ rendered a white solid which was filtered, washed with Et_2O (3×3 cm^3) and vacuum dried (45 mg, 58 μ mol, 63% yield). The compound thus obtained was identified as $[PPh_4][(CF_3)_3AuCl]$.^[24]

Synthesis of $[PPh_4][(CF_3)_3AuBr]$: To a solution of compound **1** (92 μ mol) in Et_2O/n -hexane (5 and 15 cm^3 , respectively) prepared as described above was added $[PPh_4]Br$ (39 mg, 92 μ mol). The resulting mixture was stirred for 30 min. and then concentrated to dryness. Treatment of the resulting residue with $iPrOH$ (3 cm^3) at $-30^{\circ}C$ rendered a white solid which was filtered, washed with Et_2O (3×3 cm^3) and vacuum dried (47 mg, 57 μ mol, 62% yield). The compound thus obtained was identified as $[PPh_4][(CF_3)_3AuBr]$.^[24]

Reversion to $[PPh_4][(CF_3)_3Au]$: Addition of $[PPh_4]I$ (6.6 mg, 13.8 μ mol) to a CD_2Cl_2 solution of **2** (13.8 μ mol), produced the quantitative reversal to the starting material $[PPh_4][(CF_3)_3Au]$ (^{19}F NMR).^[24]

Computational Details: Quantum mechanical calculations were performed with the Gaussian09 package at the DFT/M06 level of theory. SDD basis set and its ECP's together with additional f-type polarization functions were used to describe Au atoms. Light atoms (H, C, N, O, F, Si, P, and S) were described with a 6-31G** basis set. See Supporting Information for full details and references.

X-Ray Structure Determinations: Crystal data and other details of the structure analyses are presented in Tables S1 and S2. Suitable crystals for X-ray diffraction studies were obtained as indicated in the appropriate experimental section. Details on the diffraction data collection and resolution are to be found in the Supporting Information.

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Keywords: gold • ligand affinity • organogold chemistry • strong Lewis acids • trifluoromethyl compounds

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**$(CF_3)_3Au$ as a Highly Acidic
Organogold(III) Fragment**

Fluorination of trimethylgold, $(CH_3)_3Au$, causes a substantial increase in the Lewis acidity of the Au center. The single-site perfluorinated $(CF_3)_3Au$ moiety arguably features the highest Lewis acidity of any conceivable R_3Au organogold species.