[2,4,6-Tris(trifluoromethyl)phenyl]gold(I) and -gold(III) Complexes

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The complex [Au(Fmes)(tht)] (Fmes = 2,4,6-tris(trifluoromethyl)phenyl or nonafluoromesityl; tht = tetrahydrothiophene) was obtained by reaction of [AuCl(tht)] and Li(Fmes). Monoarylated complexes are readily obtained when the tht ligand is displaced by other neutral ligands, giving [Au(Fmes)L] (L = PPh_3, P(*o*-tol)$_3$, 2,6-lutidine) or [Au_2(Fmes)$_2$(μ-bipy)] (bipy = 2,2′-bipyridyl), the latter containing a bridging bipy ligand. tht can also be displaced by halides to give the gold anionic complexes NBu_4[Au(Fmes)X] (X = Cl, Br, I). [Au(Fmes)(NCMe)] is obtained from the latter by treatment with $TlBF_4$ in the presence of MeCN. The bis-arylated complexes NR_4[Au(Fmes)$_2$] (R = Et, Bu) were obtained by treatment of NR_4[$AuBr_2$] with excess Li(Fmes). They react with $AgBF_4$ and 4-methylpyridine to give [Ag(4-Mepy)$_2$][Au(Fmes)$_2$]. Oxidative addition of halogens to the monoarylated NBu_4[Au(Fmes)X] and the bis-arylated NR_4[Au(Fmes)$_2$] gives the gold(III) complexes NBu_4[Au(Fmes)X_3] and NR_4[*trans*-Au(Fmes)$_2X_2$], respectively. The structures of the bis-arylated gold(I) and -(III) complexes NBu_4[Au(Fmes)$_2$] and NEt_4[*trans*-Au(Fmes)$_2I_2$] were determined by X-ray diffraction. An analysis of nonbonded distances and torsion angles suggests that steric repulsion of neighboring CF_3 groups is reduced by mutual rotation of the Fmes rings in the former complex but by rotation of the CF_3 groups themselves in the latter (in which the Fmes rings are exactly coplanar).

Introduction

The use of fluoroaryl ligands has facilitated the rapid development of the organometallic chemistry of gold.[1] The higher stability of fluoroaryl, as compared to aryl, complexes can be attributed to the higher electronegativity of fluoroaryl ligands, which introduces some ionic character into the M−C bond and probably some M-to-C π back-donation,[2] and also to the fact that F-elimination is disfavored for late transition elements, in contrast to the favorable H-elimination.[3] The 2,4,6-tris(trifluoromethyl)phenyl ligand (nonafluoromesityl or Fmes) shares these features to some extent, but in addition it presents specific properties associated with its high steric demand. Thus, it can favor lower coordination numbers, hinder rotation of the ligands, offer a high degree of axial protection in square-planar complexes,[4] or involve its *o*-CF_3 groups in M···F interactions.[5]

These properties have made Fmes an interesting ligand for main-group elements, where it stabilizes low-valent or low-coordinated complexes. Thus, Fmes complexes are known for group 13,[6] group 14,[7] and Bi[8] and also for group 12 elements,[9] whereas transition-metal complexes have been reported for V,[10] Cr, Mo,[11] Re,[5] Co,

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Scheme 1. Equilibrium Detected in Solution for 1

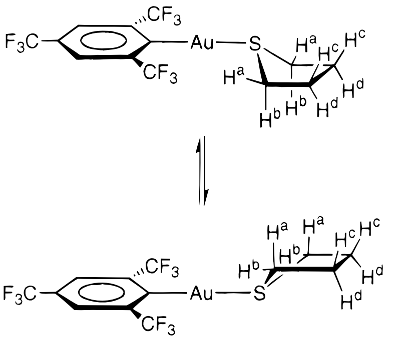
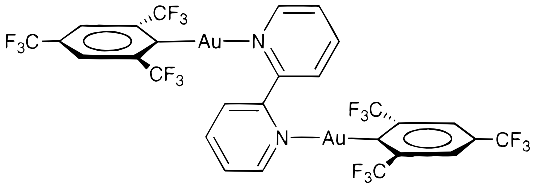


Chart 1. Structure Proposed for 4



Ni,[12] and Pd.[4] The only group 11 derivative reported so far is Cu(Fmes), which was not isolated as a solid.[9a] Herein we report the synthesis and characterization of the first Au(I) and Au(III) complexes of Fmes, including standard structural types and precursors in gold chemistry.

Results and Discussion

Gold(I) Complexes. All the monoarylated gold(I) complexes were obtained from the general precursor [Au(Fmes)(tht)] (**1**), which was synthesized from [AuCl-(tht)] and excess Li(Fmes). The ^{1}H NMR spectrum of **1** reveals two broad signals displayed by the tht protons at room temperature, which split into two multiplets at −60 °C. This can be related to a slow inversion of the tht ring and the sulfur coordination, as shown in Scheme 1, causing the exchanges H^a−H^b and H^c−H^d. The ^{19}F NMR spectrum displays a singlet for the *o*-CF_3 even at the lowest temperature, compatible either with free rotation of the Fmes group around the Au−C bond or with a parallel arrangement of Fmes and tht as depicted in Scheme 1.

Complex **1** is a good precursor for monoarylated gold-(I) complexes, since tht is easily replaced by other ligands. The reactions with PPh_3 or P(*o*-tol)$_3$ took place readily at room temperature in dichloromethane, yielding [Au(Fmes)(PR_3)] (R = Ph (**2a**), *o*-tol (**2b**)). When equimolar amounts of **1** and 2,6-lutidine (lut) were refluxed, [Au(Fmes)(lut)] (**3**) was obtained, which does not show any sign of fluxionality in the NMR spectra, suggesting a rigid structure with the two rings perpendicular to each other in order to diminish crowding. With 2,2′-bipyridine (bipy), [Au_2(Fmes)$_2$(*μ*-bipy)] (**4**), containing a bridging bipy group (Chart 1), was obtained regardless of the Au:bipy ratio used (1:1 or 2:1).

Complexes with poorer donor ligands than tht, such as [Au(Fmes)(NCMe)] (**5**), can be obtained by removing halogen from the complexes NBu_4[Au(Fmes)X] with $TlBF_4$, in the presence of the desired ligand.

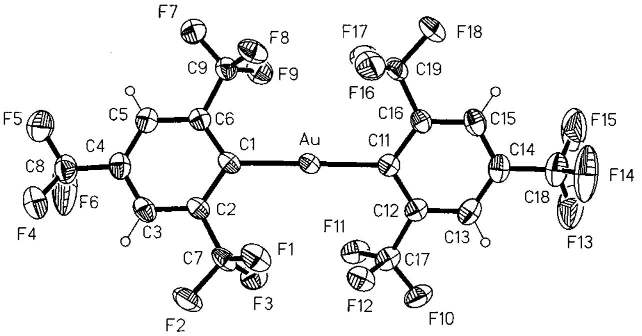


Figure 1. Molecular structure of the anion of **7a** showing the atom-numbering scheme. The ellipsoids are drawn at the 50% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 7a

Au−C(1)	2.060(5)	Au−C(11)	2.057(5)
C(1)−Au−C(11)	178.2(2)	C(16)−C(11)−C(12)	113.2(5)
C(6)−C(1)−C(2)	113.4(5)		

The mono-arylated anionic complexes NBu_4[Au-(Fmes)X] (X = Cl (**6a**), Br (**6b**), I (**6c**)), were synthesized in good yields by reacting **1** with equimolar amounts of the respective NBu_4X species in CH_2Cl_2. An alternative method uses the bis-arylated complexes as arylating reagents (eq 1). Since the transmetalation is quantita-

$$NBu_4[Au(Fmes)_2] + NBu_4[AuBr_2] \rightarrow 2NBu_4[Au(Fmes)Br] \quad (1)$$

tive and the bis-arylated compounds are obtained in good yield, this is also a convenient synthetic method.

The bis-arylated complexes NR_4[Au(Fmes)$_2$], (R = Bu (**7a**), Et (**7b**)) were obtained from the respective NR_4-[$AuBr_2$] and excess Li(Fmes). A 1:4 ratio was used in order to avoid mixtures with the monoarylated anions [Au(Fmes)Br]$^-$, which are difficult to separate.

The reaction of **7b** with $AgBF_4$ was carried out in order to determine whether it could bring about linear polymers [{$AuAgR_2$}$_n$] or [{$AgAuR_2L$}$_n$] similar to those reported for R = C_6F_5.[13] However, neither of these polymeric species could be found, and only low yields of [Ag(4-Mepy)$_2$][Au(Fmes)$_2$] (**7c**) could be obtained after addition of 4-methylpyridine in either a 1:1 or 1:2 ratio. Similar complexes have also been described for C_6F_5.[13]

A crystallographic study of the bis-arylated complex **7a** was carried out in order to determine whether the bulkiness of the ligand affects the geometry of the molecule compared to the case for less hindered aryl complexes. Figure 1 shows a thermal ellipsoid plot of the anion, with selected bonds and angles given in Table 1. The anion shows the expected linear coordination for gold(I), with C−Au−C = 178.2(2)°. The Au−C distances (2.057, 2.060(5) Å) are essentially equal and are similar to related distances in other arylgold complexes.[1,14] Also, the angles at the *ipso* carbons (113.3, 113.1(5)°) are equal and similar to those found in gold C_6F_5 deriva-

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tives[15] or in palladium Fmes derivatives;[4] the narrowness of these formally sp^2 angles may be attributed to electronegativity differences.[15]

It is clear that complexes bearing two Fmes ligands are sterically congested in the region of the metal center and the *o*-CF$_3$ groups; in general, steric strain may be reduced by rotation of the affected groups (here the Fmes rings or the individual CF$_3$ groups) away from each other or by relaxation of bond lengths and angles. The latter, however, tend to be "harder" parameters. The most striking feature of **7a** is the twist angle defined by the ring planes of the two Fmes ligands, which is 27.2(2)°, whereas other [Au(aryl)$_2$]$^-$ complexes are planar.[14] There is no clear evidence for elongation of the Au−C distances or further narrowing of C(*ipso*) angles, and thus the steric crowding around the metal center seems to be sufficiently alleviated by laterally displacing the four *o*-CF$_3$ groups, which would collide frontally in a planar arrangement (considering only the first Fmes ligand and imposing inversion symmetry at the Au atom, the distance between F1 and F9′ would be only 2.66 Å). In fact, the shortest F···F nonbonding distances are 2.822 Å (F3···F12) and 2.910 Å (F9···F17), slightly shorter than the sum of van der Waals radii (ca. 3.0 Å).[16] The distances between the gold atom and the closest fluorine atoms of the *o*-CF$_3$ substituents are in the narrow range 3.166 Å (Au···F1) to 3.303 Å (Au···F3), which is approximately the sum of the van der Waals radii (3.30 Å); thus, appreciable attractive Au−F interactions need not be postulated, as was also the case in Fmes complexes of palladium(II).[4] These distances are correlated with the torsion angles C(*ipso*)−C(*ortho*)−C−F; the greater the distance, the greater the torsion angle (and also the displacement of the fluorine from the Fmes ring plane). For **7a**, the largest difference in absolute torsion angles within an *o*-CF$_3$ group is 16° (53° for F1, 69° for F3; cf. 3.17, 3.30 Å for the corresponding Au···F distances). To summarize, the steric strain is relaxed by mutual rotation of the Fmes planes, whereas the *o*-CF$_3$ groups remain symmetrically disposed with respect to those planes. Some degree of steric locking of these groups (which under other circumstances generally display a high tendency to rotational disorder) is indicated by the relatively low U values of the relevant F atoms (mean $U_{eq} = 0.051$ Å^2), in contrast to the *p*-CF$_3$ groups (mean $U_{eq} = 0.102$ Å^2), which show considerable apparent rotation about the C−C bond.

Gold(III) Complexes. The reactions of complexes **6** with halogens gave the gold(III) monoarylated anionic complexes NBu$_4$[Au(Fmes)X$_3$] (X = Cl (**8a**), Br (**8b**), I (**8c**)). Somewhat to our surprise, since we expected steric protection, the bis-arylated gold(III) complexes NR$_4$-[*trans*-Au(Fmes)$_2$X$_2$] (R = Bu, X = Cl (**9a**), Br (**9b**), I (**9c**); R = Et, X = I (**9d**)) were easily obtained by halogenation of complexes **7**, even with the bulky I$_2$. Spectroscopic and conductivity data for the complexes are given in the experimental part. The *trans* geometry proposed for the bis-aryl complexes **9** is based on the X-ray crystallographic determination of the diiodo complex **9d**, which was chosen for this study because it was expected to show the greatest crowding.

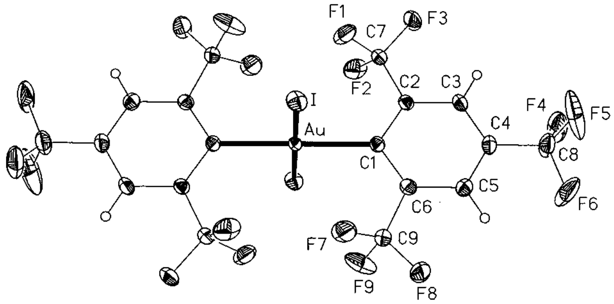

Figure 2. Molecular structure of the anion of **9d** showing the atom-numbering scheme. The ellipsoids are drawn at the 50% probability level.

Table 2: Selected Bond Lengths (Å) and Angles (deg) for 9d

Au−C(1)	2.098(2)	Au−I	2.6139(2)
C(1)−Au−C(1)#1	180.0	I−Au−I#1	180.0
C(1)−Au−I#1	90.92(6)	C(1)−Au−I	89.08(6)
C(6)−C(1)−C(2)	115.4(2)		

The structure of the anion is shown in Figure 2, with selected distances and angles given in Table 2. The anion is centrosymmetric, with exactly planar coordination at the gold(III) center. The Au−C distances (2.098(2) Å) are noticeably longer than in **7a**, whereas the angles at the *ipso* carbons, 115.4(2)°, are only slightly larger. The Au−I distances are equal by symmetry (2.6139(2) Å) and slightly longer than those found in the noncrowded gold(III) derivative [Au{C(NHAr)$_2$}I$_2$]ClO$_4$ (2.601(2) and 2.606(2) Å).[17] The angle between the coordination plane and the Fmes ring is 89.5°. In contrast to the case for **7a**, the Fmes rings in **9d** are exactly coplanar (by virtue of the imposed symmetry). However, the Au···F$_3$C(*ortho*) nonbonding distances vary over an appreciably larger range (3.062 Å (Au···F7) to 3.516 Å (Au···F9)) than in **7a**; correspondingly, the C−C−C−F torsion angles also vary more (53, 69, 49, and 72° for F1, F2, F7, and F9 respectively). The shortest F···F contacts are 2.840 Å for F2···F7′ and 2.976 Å for F1···F9′. It may be concluded that steric strain is reduced by a rotation of the *o*-CF$_3$ groups rather than of the Fmes rings (as in **7a**). A possible reason for this may be sought in the nonbonding distances F···I (3.421 Å for I···F9 and 3.455 Å for I···F1), which are slightly shorter than the sum of van der Waals radii (ca. 3.5 Å),[16] suggesting that incorporation of the two iodine atoms does not allow the twisting of the aryl rings because of I···CF$_3$ repulsions. The mean U_{eq} values of the F atoms (0.039 Å^2 for *ortho*, 0.087 Å^2 for *para*) are again indicative of steric anchoring effects at the *ortho* position.

It is also conceivable that the higher repulsions of the *o*-CF$_3$ substituents in the coplanar arrangement force the Au−C bonds to elongate slightly in order to diminish these interactions. A search of the Cambridge Crystallographic Database for Au−C$_6$F$_5$ complexes yielded 5 hits for the fragment Au^{I}(C$_6$F$_5$)$_2$, with Au−C = 2.042−2.094 Å (mean 2.055 Å), whereas the fragment *trans*-Au^{III}(C$_6$F$_5$)$_2$ was found 23 times with Au−C = 2.050−2.092 Å (mean 2.068 Å). This would indicate that the Au−C bond in **9d** is indeed unusually long. It remains

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unclear to what extent steric factors are responsible for this lengthening.

Experimental Section

General Comments. All reactions were carried out under N_2 atmosphere. Solvents were purified according to standard procedures.[18] [AuCl(tht)],[19] $NR_4[AuBr_2]$,[20] (R = Bu, Et) were prepared according to literature procedures. 1,3,5-$C_6H_3(CF_3)_3$ (FmesH) from Fluorochem was used as received, and Li(Fmes) was prepared in situ as described in the literature.[9a,21]

Infrared spectra were recorded in a Perkin-Elmer 883 or 1720X apparatus on Nujol mulls between polystyrene films from 4000 to 200 cm^{-1}. NMR spectra were recorded in Bruker AC-300 or ARX-300 instruments in $CDCl_3$, at room temperature unless otherwise stated. NMR spectra are referenced to TMS, $CFCl_3$, or 85% aqueous H_3PO_4. Elemental analyses were performed on a Perkin-Elmer 2400B microanalyzer. Electrical conductivity measurements were carried out at room temperature with a Crison 522 conductivimeter on ca. 5×10^{-4} M solutions; the range of molar conductivity for 1/1 electrolytes is 100−140 S cm^2 mol^{-1} in acetone solutions.[22]

[Au(Fmes)(tht)] (1). [AuCl(tht)] (0.577 g, 1.8 mmol) was added to a freshly prepared solution of Li(Fmes) (3.6 mmol) in Et_2O (20 mL). The mixture was stirred for 14 h, and then 2 drops of water were added to hydrolyze the excess of organolithium reagent. The volatiles were pumped off, and the residue was extracted with CH_2Cl_2 (50 mL) and filtered on dry Celite. Hexane (25 mL) was added to the filtrate, which was concentrated and cooled to −20 °C. The colorless crystals thus obtained were decanted, washed with hexane (3 × 5 mL), and vacuum-dried. Yield: 0.673 g (67%) of **1**. ^{19}F NMR: δ −61.0 (s, o-CF_3, 6F), −63.2 (s, p-CF_3, 3F). ^{19}F NMR (−60 °C): δ −60.7 (s, o-CF_3, 6F), −62.6 (s, p-CF_3, 3F). ^1H NMR: δ 7.99 (s, $C_6H_2(CF_3)_3$, 2H), 3.40 (br, H^2 of tht, 4H), 2.22 (br, H^3 of tht, 4H). ^1H NMR (−60 °C): δ 7.99 (s, $C_6H_2(CF_3)_3$, 2H), 3.53 (m, H^2 of tht, 2H), 3.30 (m, H^2 of tht, 2H), 2.34 (m, H^3 of tht, 2H), 2.09 (m, H^3 of tht, 2H). IR: 1623 s, 1570 m, 1299 vs, 1284 vs, 1189 vs, 1135 vs, 1109 vs, 1040 w, 959 w, 913 s, 885 w, 853 m, 835 m, 743 m, 696 m, 685 m, 668 w, 584 w, 563 w, 470 w, 329 w, 317 w, 305 w, 256 w, 247 w, 223 w, 219 w cm^{-1}. Anal. Calcd for $C_{13}H_{10}AuF_9S$: C, 27.58; H, 1.78. Found: C, 27.21; H, 1.63.

[Au(Fmes)(PPh$_3$)] (2a). PPh_3 (0.026 g, 0.1 mmol) was added to a solution of **1** (0.057 g, 0.1 mmol) in CH_2Cl_2 (10 mL), and the solution was stirred for 2 h. The volatiles were pumped off, and the residue was washed with hexane (3 × 5 mL) and recrystallized from CH_2Cl_2−hexane, giving colorless crystals of **2a**, which were decanted, washed with hexane (3 × 5 mL), and vacuum-dried. Yield: 0.053 g (72%). ^{19}F NMR: δ −60.4 (d, J_{PF} = 1 Hz, o-CF_3, 6F), −63.1 (s, p-CF_3, 3F). $^{31}P\{^1H\}$ NMR: δ 42.3 (sept). ^1H NMR: δ 8.06 (s, $C_6H_2(CF_3)_3$, 2H), 7.5 (m, C_6H_5, 15H). IR: 1622 s, 1298 vs, 1278 vs, 1192 vs, 1126 vs(sh), 1083 s, 908 s, 853 w, 835 w, 694 s, 536 m, 503 m, 469 m, 450 m(sh), 358 w, 329 m, 305 m, 234 m, 214 m cm^{-1}. Anal. Calcd for $C_{27}H_{17}AuF_9P$: C, 43.80; H, 2.31. Found: C, 43.62; H, 2.45.

[Au(Fmes)(P(*o*-tol)$_3$)] (2b). P(o-tol)$_3$ (0.036 g, 0.12 mmol) was added to a solution of **1** (0.067 g, 0.12 mmol) in CH_2Cl_2 (15 mL), and the solution was stirred for 2 h. Workup as for **2a** yielded 0.050 g (55%) of **2b** as colorless crystals. ^{19}F NMR: δ −60.6 (d, J_{PF} = 1 Hz, o-CF_3, 6F), −63.2 (s, p-CF_3, 3F). $^{31}P\{^1H\}$ NMR: δ 25.3 (sept). ^1H NMR: δ 8.01 (s, $C_6H_2(CF_3)_3$, 2H), 7.46 (m, C_6H_4Me, 3H), 7.37 (m, C_6H_4Me, 3H), 7.20 (t, J = 7.5 Hz, C_6H_4Me, 3H), 6.98 (dd, J = 12 and 7.5 Hz, C_6H_4Me, 3H), 2.69 (s, CH_3, 9H). IR: 1623 s, 1570 m, 1295 vs(sh), 1279 vs, 1264 vs, 1193 vs, 1141 vs, 1123 vs(sh), 1085 m, 1032 w, 913 s, 853 w, 836 w, 807 w, 768 s, 757 s, 746 m, 693 m, 684 m, 670 w, 602 w, 572 w, 472 s, 317 w, 305 w, 282 w, 247 w cm^{-1}. Anal. Calcd for $C_{30}H_{23}AuF_9P$: C, 46.05; H, 2.96. Found: C, 45.90; H, 2.95.

[Au(Fmes)(2,6-lut)] (3). 2,6-Lutidine (25 μL, 0.0215 g, 0.2 mmol) was added to a solution of **1** (0.113 g, 0.2 mmol) in toluene (20 mL), and the solution was refluxed for 2 h. Workup as for **2a** yielded 0.073 g (63%) of **3** as colorless crystals. ^{19}F NMR: δ −60.6 (s, o-CF_3, 6F), −63.1 (s, p-CF_3, 3F). ^1H NMR: δ 8.03 (s, $C_6H_2(CF_3)_3$, 2H), 7.75 (t, J = 7.5 Hz, $C_6H_3Me_2$, $1H^{para}$), 7.29 (m, $C_6H_3Me_2$, $2H^{meta}$), 2.94 (s, CH_3, 6H). IR: 1620 s, 1566 m, 1298 vs, 1278 vs(sh), 1176 vs(sh), 1033 m, 912 s, 853 m, 834 m, 782 s, 696 s, 684 s, 563 w, 475 w, 439 m, 329 m, 305 m, 284 w, 247 m, 217 w cm^{-1}. Anal. Calcd for $C_{16}H_{11}AuF_9N$: C, 32.84; H, 1.89; N, 2.39. Found: C, 32.91; H, 1.98; N, 2.35.

[Au$_2$(Fmes)$_2$(*μ*-bipy)] (4). 2,2′-Bipyridyl (0.016 g, 0.1 mmol) was added to a solution of **1** (0.057 g, 0.1 mmol) in toluene (10 mL), and the solution was refluxed for 2 h. Workup as for **2a** yielded 0.032 g (58%) of **4** as colorless crystals. ^{19}F NMR: δ −61.3 (s, o-CF_3, 12F), −63.2 (s, p-CF_3, 6F). ^1H NMR: δ 8.90 (d, J = 5 Hz, H^6 of bipy, 2H), 8.22 (t, J = 8 Hz, H^5 of bipy, 2H), 7.95 (d, J = 7.5 Hz, H^3 of bipy, 2H), 7.88 (s, $C_6H_2(CF_3)_3$, 4H), 7.83 (t, J = 6.5 Hz, H^4 of bipy, 2H). IR: 1624 m, 1611 w, 1570 w, 1299 vs, 1281 vs, 1192 vs, 1128 vs, 916 s, 854 w, 836 w, 786 w, 769 w, 759 w, 697 m, 685 w, 553 w, 439 w, 305 w, 247 w cm^{-1}. Anal. Calcd for $C_{28}H_{12}Au_2F_{18}N_2$: C, 30.23; H, 1.09; N, 2.52. Found: C, 29.98; H, 1.22; N, 2.70.

[Au(Fmes)(NCMe)] (5). A 100 mL flask was successively charged with $NBu_4[Au(Fmes)Cl]$ (**6a**; 0.076 g, 0.1 mmol), Et_2O (10 mL), MeCN (0.5 mL), and $TlBF_4$ (0.032 g, 0.11 mmol), and the mixture was stirred for 8 h. The solution was then filtered under nitrogen, the solvents were pumped off, and the residue was extracted with Et_2O (5 × 5 mL). Hexane (10 mL) was added to this solution, which was concentrated and cooled to −20 °C. The colorless crystals thus obtained were decanted, washed with hexane (2 × 3 mL), and vacuum-dried, yielding 0.024 g (46%) of **5**. ^{19}F NMR: δ −61.1 (s, o-CF_3, 6F), −63.3 (s, p-CF_3, 6F). ^1H NMR: δ 7.97 (s, $C_6H_2(CF_3)_3$, 2H), 2.39 (s, CH_3-CN, 3H). IR: 2335 m, 2309 w, 1623 m, 1571 w, 1300 vs, 1286 vs, 1269 s, 1185 vs, 1125 vs, 915 s, 855 m, 836 m, 684 m, 667 w, 585 w, 477 w, 439 w, 305 w, 292 w cm^{-1}. Anal. Calcd for $C_{11}H_5AuF_9N$: C, 25.45; H, 0.97; N, 2.70. Found: C, 25.61; H, 1.03; N, 2.65.

NBu$_4$[Au(Fmes)Cl] (6a). NBu_4Cl (0.124 g, 0.45 mmol) was added to a solution of **1** (0.253 g, 0.45 mmol) in CH_2Cl_2 (20 mL), and the solution was stirred for 2 h. The volatiles were pumped off, and the white residue was recrystallized from Me_2CO−EtOH at −20 °C, giving colorless needles of **6a**, which were decanted, washed with Et_2O (3 × 5 mL), and vacuum-dried. Yield: 0.228 g (67%). ^{19}F NMR: δ −60.7 (s, o-CF_3, 6F), −63.0 (s, p-CF_3, 3F). ^1H NMR: δ 7.92 (s, $C_6H_2(CF_3)_3$, 2H), 3.24 (m, CH_2, 8H), 1.61 (m, CH_2, 8H), 1.41 (sext, J = 7.5 Hz, CH_2, 8H), 0.95 (t, J = 7.5 Hz, CH_3, 12H). IR: 1621 s, 1567 m, 1297 vs, 1280 vs, 1263 vs(sh), 1188 vs, 1149 vs(sh), 1118 vs, 1086 m, 1040 m, 1024 m, 911 s, 884 m, 854 m, 833 m, 796 w, 696 m, 684 s, 668 m, 560 w, 473 w, 439 w, 358 w, 328 m(sh), 305 m, 283 w, 247 m, 234 w, 229 w, 214 m cm^{-1}. Anal. Calcd for $C_{25}H_{38}AuClF_9N$: C, 39.72; H, 5.07; N, 1.85. Found: C, 39.70; H, 4.95; N, 1.87. Conductivity: $\Lambda_M(Me_2CO)$ = 119 S cm^2 mol^{-1}.

NBu$_4$[Au(Fmes)Br] (6b). Method A. NBu_4Br (0.097 g, 0.3 mmol) was added to a solution of **1** (0.170 g, 0.3 mmol) in CH_2Cl_2 (20 mL), and the solution was stirred for 2 h. Workup as for **6a** yielded 0.165 g (69%) of **6b** as colorless needles.

Method B. A 100 mL flask was successively charged with $NBu_4[Au(Fmes)_2]$ (**7a**; 0.100 g, 0.1 mmol), $NBu_4[AuBr_2]$ (0.060 g, 0.1 mmol), and MeCN (10 mL), and the mixture was stirred at 60 °C for 24 h. Workup as for **6a** yielded 0.102 g (63%) of **6b**. ^{19}F NMR: δ −60.7 (s, o-CF_3, 6F), −63.0 (s, p-CF_3, 3F). ^1H

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NMR: δ 7.93 (s, $C_6H_2(CF_3)_3$, 2H), 3.22 (m, CH_2, 8H), 1.61 (m, CH_2, 8H), 1.37 (sext, $J = 7.5$ Hz, CH_2, 8H), 0.95 (t, $J = 7.5$ Hz, CH_3, 12H). IR: 1621 m, 1567 w, 1297 vs, 1280 vs, 1263 vs, 1180 vs, 1118 vs, 911 m, 884 w, 853 w, 833 w, 684 m, 562 w, 441 w, 337 w, 305 m, 282 m, 247 w, 232 w, 218 m cm^{-1}. Anal. Calcd for $C_{25}H_{38}AuBrF_9N$: C, 37.51; H, 4.79; N, 1.75. Found: C, 37.75; H, 4.66; N, 1.79. Conductivity: $\Lambda_M(Me_2CO) = 112$ S cm^2 mol^{-1}.

$NBu_4[Au(Fmes)I]$ (6c). NBu_4I (0.055 g, 0.15 mmol) was added to a solution of **1** (0.085 g, 0.15 mmol) in CH_2Cl_2 (15 mL), and the solution was stirred for 2 h. Workup as for **6a** yielded 0.062 g (50%) of **6c** as colorless needles. ^{19}F NMR: δ −60.6 (s, o-CF_3, 6F), −63.0 (s, p-CF_3, 3F). ^{1}H NMR: δ 7.96 (s, $C_6H_2(CF_3)_3$, 2H), 3.20 (m, CH_2, 8H), 1.61 (m, CH_2, 8H), 1.36 (sext, $J = 7.5$ Hz, CH_2, 8H), 0.95 (t, $J = 7.5$ Hz, CH_3, 12H). IR: 1619 s, 1565 m, 1295 vs(sh), 1277 vs(sh), 1184 vs, 1131 vs, 1082 vs, 1031 s, 908 s, 885 s, 853 m, 833 m, 800 w, 694 m, 684 w, 668 w, 604 w, 470 m, 440 m, 378 w, 329 m, 305 m, 283 w, 247 m, 229 m(sh), 211 s, 208 m cm^{-1}. Anal. Calcd for $C_{25}H_{38}AuF_9IN$: C, 35.53; H, 4.52; N, 1.65. Found: C, 35.33; H, 4.41; N, 1.52. Conductivity: $\Lambda_M(Me_2CO) = 129$ S cm^2 mol^{-1}.

$NBu_4[Au(Fmes)_2]$ (7a). $NBu_4[AuBr_2]$ (0.584 g, 0.97 mmol) was added to a recently prepared solution of Li(Fmes) (3.9 mmol) in 20 mL of Et_2O. The mixture was stirred for 22 h. Workup as for **1** yielded 0.820 g (84%) of **7a** as colorless needles. ^{19}F NMR: δ −60.3 (s, o-CF_3, 12F), −62.9 (s, p-CF_3, 6F). ^{1}H NMR: δ 7.97 (s, $C_6H_2(CF_3)_3$, 4H), 2.86 (m, CH_2, 8H), 1.34 (m, CH_2, 8H), 1.10 (sext, $J = 7.5$ Hz, CH_2, 8H), 0.83 (t, $J = 7.5$ Hz, CH_3, 12H). IR: 1619 s, 1563 m, 1281 vs, 1187 vs, 1168 vs, 1143 vs, 1122 vs, 1075 m, 930 w, 914 s, 884 w, 852 w, 834 m, 800 m, 756 w, 685 s, 670 w, 565 w, 441 w, 337 w, 305 m, 283 m, 220 m cm^{-1}. Anal. Calcd for $C_{34}H_{40}AuF_{18}N$: C, 40.77; H, 4.02; N, 1.40. Found: C, 40.68; H, 4.00; N, 1.47. Conductivity: $\Lambda_M(Me_2CO) =105$ S cm^2 mol^{-1}.

$NEt_4[Au(Fmes)_2]$ (7b). $NEt_4[AuBr_2]$ (0.497 g, 1.02 mmol) was added to a recently prepared solution of Li(Fmes) (4.1 mmol) in 20 mL of Et_2O. The mixture was stirred for 22 h. Workup as for **1** yielded 0.371 g (42%) of **7b** as colorless crystals. ^{19}F NMR: δ −60.4 (s, o-CF_3, 12F), −62.9 (s, p-CF_3, 6F). ^{1}H NMR: δ 7.98 (s, $C_6H_2(CF_3)_3$, 4H), 2.93 (q, $J = 7.5$ hz, CH_2, 8H), 1.05 (m, CH_3, 12H). Anal. Calcd for $C_{26}H_{24}AuF_{18}N$: C, 35.11; H, 2.72; N, 1.57. Found: C, 34.96; H, 2.65; N, 1.68.

$[Ag(4\text{-}Mepy)_2][Au(Fmes)_2]$ (7c). A 100 mL flask was successively charged with $AgBF_4$ (0.082 g, 0.42 mmol), CH_2Cl_2 (20 mL), and **7b** (0.356 g, 0.40 mmol), and the mixture was stirred for 1 h, during which time metallic deposition was observed. Then 4-methylpyridine (86 μL, 0.082 g, 0.88 mmol) was added and the mixture was stirred for 5 h. The volatiles were pumped off, the residue was washed with hexane (3 × 10 mL) and then extracted with Et_2O (3 × 10 mL), and the extracts were filtered. Hexane (30 mL) was added to the filtrate, which was concentrated and cooled to −20 °C. The colorless crystals obtained were decanted, washed with hexane (3 × 5 mL), and vacuum-dried. Yield: 0.139 g (33%) of **7c**. The solid residue was extracted with CH_2Cl_2, the solvent was removed, and the residue was identified as NEt_4BF_4 by ^{1}H and ^{19}F NMR. ^{19}F NMR: δ −60.9 (s, o-CF_3, 12F), −63.1 (s, p-CF_3, 6F). ^{1}H NMR: δ 8.44 (d, $J = 6.5$ Hz, H^2 of 4-CH_3py, 4H), 7.99 (s, $C_6H_2(CF_3)_3$, 4H), 7.39 (d, $J = 6.5$ Hz, H^3 of 4-CH_3py, 4H), 2.48 (s, 4-CH_3py, 6H). IR: 1621 s, 1568 w, 1280 vs, 1230 vs, 1187 vs, 1072 w, 1044 w, 931 w, 915 s, 854 m, 834 m, 809 s, 697 m, 685 s, 583 w, 563 w, 491 m, 474 w, 441 m cm^{-1}. Anal. Calcd for $C_{30}H_{18}AgAuF_{18}N_2$: C, 34.21; H, 1.72; N, 2.66. Found: C, 33.96; H, 1.67; N, 2.69.

$NBu_4[Au(Fmes)Cl_3]$ (8a). A 0.81 M solution of Cl_2 in CCl_4 (0.247 mL, 0.2 mmol) was added to a solution of **6a** (0.075 g, 0.1 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 2 h. The volatiles were removed under vacuum, and the white residue was recrystallized from Et_2O−hexane at −20 °C, giving off-white crystals of **8a**, which were decanted, washed with hexane (3 × 5 mL), and vacuum-dried. Yield: 0.035 g (43%). ^{19}F NMR: δ −58.2 (s, o-CF_3, 6F), −63.4 (s, p-CF_3, 3F). ^{1}H NMR: δ 7.96 (s, $C_6H_2(CF_3)_3$, 2H), 3.25 (m, CH_2, 8H), 1.66 (m, CH_2, 8H), 1.47 (sext, $J = 7.5$ Hz, CH_2, 8H), 1.03 (t, $J = 7.5$ Hz, CH_3, 12H). IR: 1619 s, 1581 w, 1299 s, 1281 vs, 1264 s, 1200 vs, 1142 vs, 1089 m, 1030 m, 911 s, 856 w, 837 w, 685 m, 585 w, 470 w, 450 w, 357 m, 305 m, 283 w, 247 w, 220 w cm^{-1}. Anal. Calcd for $C_{25}H_{38}AuCl_3F_9N$: C, 36.31; H, 4.63; N, 1.69. Found: C, 36.51; H, 4.34; N, 1.79. Conductivity: $\Lambda_M(Me_2CO) = 117$ S cm^2 mol^{-1}.

$NBu_4[Au(Fmes)Br_3]$ (8b). Br_2 (20.6 μL, 0.064 g, 0.4 mmol) was added to a solution of **6b** (0.151 g, 0.2 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 2 h. Workup as for **8a** yielded 0.121 g (62%) of **8b** as intense yellow needles. ^{19}F NMR: δ −57.7 (s, o-CF_3, 6F), −63.3 (s, p-CF_3, 3F). ^{1}H NMR: δ 7.95 (s, $C_6H_2(CF_3)_3$, 2H), 3.26 (m, CH_2, 8H), 1.68 (m, CH_2, 8H), 1.48 (sext, $J = 7.5$ Hz, CH_2, 8H), 1.04 (t, $J = 7.5$ Hz, CH_3, 12H). IR: 1620 m, 1582 w, 1300 vs, 1287 vs, 1262 s, 1190 vs, 1137 vs, 1091 w, 1028 w, 912 m, 891 w, 837 w, 683 m, 469 w, 305 w, 283 w, 256 m, 242 w, 223 w, 219 m cm^{-1}. Anal. Calcd for $C_{25}H_{38}AuBr_3F_9N$: C, 31.27; H, 3.99; N, 1.46. Found: C, 37.41; H, 3.74; N, 1.39. Conductivity: $\Lambda_M(Me_2CO) = 119$ S cm^2 mol^{-1}.

$NBu_4[Au(Fmes)I_3]$ (8c). I_2 (0.048 g, 0.19 mmol) was added to a solution of **6c** (0.079 g, 0.094 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 2 h. The volatiles were pumped off, and the unreacted iodine was extracted with hexane (5 × 5 mL). The residue was recrystallized from Et_2O−hexane at −20 °C, giving black needles of **8c**, which were decanted, washed with hexane (3 × 5 mL), and vacuum-dried. Yield: 0.063 g (60%). ^{19}F NMR: δ −57.4 (s, o-CF_3, 6F), −63.1 (s, p-CF_3, 3F). ^{1}H NMR: δ 7.94 (s, $C_6H_2(CF_3)_3$, 2H), 3.26 (m, CH_2, 8H), 1.70 (m, CH_2, 8H), 1.50 (sext, $J = 7.5$ Hz, CH_2, 8H), 1.05 (t, $J = 7.5$ Hz, CH_3, 12H). IR: 1618 m, 1578 w, 1297 s, 1279 vs, 1194 vs, 1138 s, 1086 m, 1021 m, 914 m, 879 w, 854 w, 835 w, 584 w, 466 w, 435 w, 337 w, 317 w, 305 m, 292 w, 246 m, 229 w cm^{-1}. Anal. Calcd for $C_{25}H_{38}AuF_9I_3N$: C, 27.27; H, 3.48; N, 1.27. Found: C, 27.42; H, 3.35; N, 1.45. Conductivity: $\Lambda_M(Me_2CO) = 106$ S cm^2 mol^{-1}.

$NBu_4[Au(Fmes)_2Cl_2]$ (9a). A 0.81 M solution of Cl_2 in CCl_4 (0.370 mL, 0.3 mmol) was added to a solution of **7a** (0.150 g, 0.15 mmol) in CH_2Cl_2 (15 mL), and the mixture was stirred for 2 h. The volatiles were pumped off, and the white residue was recrystallized from CH_2Cl_2−hexane at −20 °C, giving colorless crystals of **9a**, which were decanted, washed with hexane (3 × 5 mL), and vacuum-dried. Yield: 0.077 g (51%). ^{19}F NMR: δ −58.9 (s, o-CF_3, 12F), −63.2 (s, p-CF_3, 6F). ^{1}H NMR: δ 7.98 (s, $C_6H_2(CF_3)_3$, 4H), 2.95 (m, CH_2, 8H), 1.45 (m, CH_2, 8H), 1.25 (sext, $J = 7$ Hz, CH_2, 8H), 0.90 (t, $J = 7$ Hz, CH_3, 12H). IR: 1621 m, 1299 vs, 1284 vs, 1160 vs, 1179 s, 1078 m, 1028 m, 917 s, 855 w, 839 w, 796 w, 761 w, 686 m, 670 w, 551 m, 441 m, 423 m, 358 w, 328 w, 316 w, 305 m, 292 m, 282 m, 268 w, 247 m, 223 w cm^{-1}. Anal. Calcd for $C_{34}H_{40}AuCl_2F_{18}N$: C, 38.07; H, 3.76; N, 1.31. Found: C, 38.30; H, 3.57; N, 1.16. Conductivity: $\Lambda_M(Me_2CO) = 122$ S cm^2 mol^{-1}.

$NBu_4[Au(Fmes)_2Br_2]$ (9b). Br_2 (15.5 μL, 0.048 g, 0.3 mmol) was added to a solution of **7a** (0.150 g, 0.15 mmol) in CH_2Cl_2 (15 mL), and the solution was stirred for 2 h. Workup as for **9a** yielded 0.097 g (52%) of **9b** as yellow crystals. ^{19}F NMR: δ −58.5 (s, o-CF_3, 12F), −63.2 (s, p-CF_3, 6F). ^{1}H NMR: δ 7.98 (s, $C_6H_2(CF_3)_3$, 4H), 2.98 (m, CH_2, 8H), 1.49 (m, CH_2, 8H), 1.29 (sext, $J = 7.5$ Hz, CH_2, 8H), 0.93 (t, $J = 7.5$ Hz, CH_3, 12H). IR: 1620 s, 1576 w, 1301 vs, 1282 vs(sh), 1192 vs, 1179 vs, 1154 vs, 1128 vs, 1104 vs, 1077 s, 1026 m, 916 s, 884 m, 839 m, 759 w, 687 s, 670 w, 667 w, 442 w, 305 m, 283 w, 256 w, 217 m cm^{-1}. Anal. Calcd for $C_{34}H_{40}AuBr_2F_{18}N$: C, 35.16; H, 3.47; N, 1.21. Found: C, 35.22; H, 3.36; N, 1.15. Conductivity: $\Lambda_M(Me_2CO) = 125$ S cm^2 mol^{-1}.

$NBu_4[Au(Fmes)_2I_2]$ (9c). I_2 (0.076 g, 0.3 mmol) was added to a solution of **7a** (0.150 g, 0.15 mmol) in CH_2Cl_2 (15 mL), and the solution was stirred at room temreratu re over 2 h. The volatiles were pumped off, and the unreacted iodine was

Table 3. Crystal Data and Structure Refinement Details for 7a and 9d

	7a	9d
empirical formula	$C_{34}H_{40}AuF_{18}N$	$C_{26}H_{24}AuF_{18}I_2N$
fw	1001.64	1143.23
temp, K	173(2) K	143(2) K
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
unit cell dimensions		
a, Å	9.436(2)	9.1804(8)
b, Å	9.490(2)	13.2607(12)
c, Å	21.472(2)	13.3327(12)
α, deg	96.35(2)	90
β, deg	93.53(2)	90.890(3)
γ, deg	92.59(2)	90
V, Å^3	1904.8(6)	1622.9(3)
Z	2	2
density (calcd), Mg/m^3	1.746	2.339
abs coeff, mm^{-1}	3.976	6.559
cryst size. mm^3	0.70 × 0.22 × 0.10	0.23 × 0.19 × 0.14
θ(max), deg	28.25	30.00
index ranges	$-9 \le h \le 12$ $-9 \le k \le 12$ $-28 \le l \le 27$	$-12 \le h \le 12$ $-18 \le k \le 18$ $-18 \le l \le 11$
no. of rflns collected	12552	13287
no. of indep rflns	8856 (*R*(int) = 0.0363)	4738 (*R*(int) = 0.0208)
max and min transmissn	0.999 and 0.364	0.945 and 0.747
no. of data/restraints/ params	8856/62/487	4738/190/216
goodness of fit on F^2	0.982	1.027
wR2 (all data)	0.098	0.046
R1 ($I > 2\sigma(I)$)	0.0435	0.0197
largest diff peak and hole, e/Å^3	1.74 and −2.96	0.985 and −0.781

extracted with hexane (5 × 5 mL). The residue was recrystallized from CH_2Cl_2−hexane at −20 °C, giving orange crystals of **9c**, which were decanted, washed with hexane (3 × 5 mL), and vacuum-dried. Yield: 0.105 g (56%). ^{19}F NMR: δ −58.2 (s, *o*-C*F*$_3$, 12F), −63.1 (s, *p*-C*F*$_3$, 6F). ^{1}H NMR: δ 7.98 (s, $C_6H_2(CF_3)_3$, 4H), 3.02 (m, C*H*$_2$, 8H), 1.50 (m, C*H*$_2$, 8H), 1.34 (sext, *J* = 7.5 Hz, C*H*$_2$, 8H), 0.96 (t, *J* = 7.5 Hz, C*H*$_3$, 12H). IR: 1621 s, 1575 w, 1283 vs, 1190 vs, 1165 vs, 1146 vs, 1077 s, 1024 m, 914 s, 855 m, 839 m, 755 m, 692 m, 686 s, 441 w, 305 w, 268 w, 241 w cm^{-1}. Anal. Calcd for $C_{34}H_{40}AuF_{18}I_2N$: C, 32.53; H, 3.21; N, 1.12. Found: C, 32.56; H, 3.01; N, 1.10. Conductivity: Λ_M (Me_2CO) = 114 S cm^2 mol^{-1}.

$NEt_4[Au(Fmes)_2I_2]$ (9d). I_2 (0.223 g, 0.88 mmol) was added to a solution of **7b** (0.393 g, 0.44 mmol) in CH_2Cl_2 (25 mL), and the solution was stirred for 2 h. Workup as for **9c** yielded 0.389 g (77%) of **9d** as orange crystals. ^{19}F NMR ($(CD_3)_2CO$): δ −57.0 (s, *o*-C*F*$_3$, 12F), −62.1 (s, *p*-C*F*$_3$, 6F). ^{1}H NMR ($(CD_3)_2CO$): δ 8.07 (s, $C_6H_2(CF_3)_3$, 4H), 3.50 (q, *J* = 7 Hz, C*H*$_2$, 8H), 1.40 (m, C*H*$_3$, 12H). Anal. Calcd for $C_{26}H_{24}AuF_{18}I_2N$: C, 27.32; H, 2.12; N, 1.23. Found: C, 27.04; H, 2.00; N, 1.34.

X-ray Crystallographic Analysis of 7a and 9d. Crystal data and refinement details for **7a** and **9d** are presented in Table 3. Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (**7a**, Siemens SMART; **9d**, Bruker SMART). Data were registered in ω-scan mode using Mo Kα radiation (λ = 0.710 73 Å). Absorption corrections were applied with the program SADABS. Structures were solved by the heavy-atom method and refined anisotropically on F^2.[23] Hydrogen atoms were included with a riding model. The cation in **9d** is disordered over an inversion center; an appropriate system of restraints (to distances and displacement parameters) was employed to ensure refinement stability.

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Supporting Information Available: Tables giving atomic positional parameters for the freely refined atoms, bond lengths and interbond angles, atomic displacement parameters, and hydrogen atom parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990435Z

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