extracted and dried on dry magnesium sulfate. Solvent evaporation followed by a silica gel column chromatography using a mixture of hexane–ether as eluant gave 130–140 mg of the tetrathiafulvalene derivative 3 (60–64%): mp 165 °C; IR (Nujol) 1743, 1715, 1575 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 60 MHz, 309 K) $\delta$ 3.93 (s, $CO_2Me$) [lit.[14] mp 169 °C; IR (KBr) 1740, 1710, 1570 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.85 (s, $CO_2Me$)].

**Preparative Electrolysis of a Mixture of Complexes 2d and 2d′.** A solution of 2 mmol of **2d** and **2d′** was first prepared by adding 2 mmol of dimethyl acetylenedicarboxylate and 2 mmol of diethyl acetylenedicarboxylate to 2850 mg (4 mmol) of **1d** in 120 mL of acetonitrile containing $LiClO_4$ (0.1 M). The electrolysis of this solution was performed at 0 V vs SCE, and the reaction products were extracted as those of the electrolysis of **2d**. A silica gel column chromatography followed by a silica gel thick-layer chromatography, using a mixture of hexane-ether as eluant, gave 110 mg of the TTF derivative 3 (12%), 140 mg of the TTF derivative 4 (15%), and 30 mg of the TTF derivative 3′ (3%).

4: IR (Nujol) 1740, 1720, 1700, 1570 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 60 MHz, 309 K) $\delta$ 4.23 (q, $OCH_2$, $^3J_{HH}$ = 7.5 Hz), 3.76 (s, $OCH_3$), 1.33 (t, $CH_3$, $^3J_{HH}$ = 7.5 Hz); MS, *m/e* calcd for $M^+(C_{16}H_{10}O_8S_4)$ 463.973, found 463.972.

3′: IR (Nujol) 1750, 1720, 1570 cm$^{-1}$; $^1$H NMR ($CDCl_3$, 60 MHz, 309 K) $\delta$ 4.13 (q, $OCH_2$, $^3J_{HH}$ = 7.5 Hz), 1.10 (t, $CH_3$, $^3J_{HH}$ = 7.5 Hz).

**Stoichiometric Oxidation of Complex 2b.** To a solution of **2b** (1 mmol) in 30 mL of $CH_2Cl_2$, prepared in situ from 464 mg of **1b** (1 mmol) and a slight excess of dimethyl acetylenedicarboxylate (0.2 mL, 1.6 mmol), was added 257 mg of silver triflate (1 mmol). The dark brown solution turned red brown with formation of a black precipitate. The solution was stirred for 1 h and then filtered on a frit. The filtrate was concentrated to 5 mL, and ether was added. On cooling to −18 °C, 490 mg of a yellow powder was obtained. Addition of 1 mmol of ferrocenium hexafluorophosphate (331 mg) instead of triflate gave the same type of salt with the $PF_6^-$ counteranion.

Anal. Calcd for $[Fe(CS_2C_2(CO_2Me)_2)(CO)_2(PMe_2Ph)_2](CF_3SO_3)(CH_2Cl_2)$ (M = 840; $C_{26}H_{28}O_9S_3P_2F_3Fe{\cdot}CH_2Cl_2$): C, 38.57; H, 3.57; S, 11.43; P, 7.38; Found: C, 38.01; H, 3.53; S, 11.87; P, 7.32. IR (Nujol): 2080, 2010, 1750 cm$^{-1}$. The NMR spectra were recorded with the sample prepared from **2b** and $Fe(C_5H_5)_2{}^+PF_6^-$ and thus containing an $PF_6^-$ anion. $^1$H NMR ($CD_3CN$, 300 MHz, 297 K): $\delta$ 7.31 (m, $C_6H_5$), 3.96, 3.92, 3.88 (s, $CO_2Me$), 2.01 (m, $PMe_2$). $^{31}$P NMR ($CD_3CN$, 32.38 MHz, 309 K): $\delta$ 21.34 (s, A), 14.54 (s, B). $^{13}C\{^1H\}$ NMR ($CD_3CN$, 75.47 MHz, 297 K): $\delta$ 273.93 (t, $Fe{=}C{<}$, $^2J_{PC}$ = 22.4 Hz, B), 263.88 (t, $Fe{=}C{<}$, $^2J_{PC}$ = 20.6 Hz, A), 214.29 (t, CO, $^2J_{PC}$ = 24.2 Hz, B), 209.81 (t, CO, $^2J_{PC}$ = 20.6 Hz, A), 208.06 (t, CO, $^2J_{PC}$ = 20.6 Hz, A). Identification of the signals due to isomer A or B is based on the relative intensity (A/B = 1/2).

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# Synthesis and Characterization of (Trifluoromethyl)gold Complexes

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The synthesis of $(CF_3)AuL$ (L = $PMe_3$, $PEt_3$, $PPh_3$) from LAuCl and $Cd(CF_3)_2{\cdot}DME$ is described. These linear gold(I) compounds readily add excess halogen to form the predominantly trans square-planar gold(III) dihalides $(CF_3)AuX_2(L)$ (X = Br, I). The use of stoichiometric (or less) halogen leads to a significant quantity of $(CF_3)_2AuX(L)$ (L = $PMe_3$, $PEt_3$) which is shown to arise from trifluoromethyl/halogen ligand exchange between $(CF_3)AuL$ and $(CF_3)AuX_2(L)$. No evidence for ligand exchange is found when L = $PPh_3$. $(CF_3)_2AuI(L)$ (L = $PMe_3$, $PEt_3$) may also be prepared in 80% yield from the oxidative addition of trifluoromethyl iodide to $(CF_3)AuL$; experiments with the radical scavenger galvinoxyl suggest a radical chain mechanism for this $CF_3I$ addition. Close examination of the $^1$H and $^{19}$F NMR spectra for the new square-planar complexes reveals that downfield shifts occur for both nuclei when a cis halide is changed from Br to I; a trans halide causes an upfield shift upon this substitution. The cadmium reagent is, in general, ineffective for the preparation of Au(III) complexes since reduction to $(CF_3)AuL$ usually occurs. However, treatment of $(CF_3)_2AuI(PMe_3)$ with $Cd(CF_3)_2{\cdot}DME$ in the presence of excess $CF_3I$ leads to the high-yield synthesis of the tris(trifluoromethyl) species $(CF_3)_3AuPMe_3$.

## Introduction

Although the first trifluoromethyl derivative of a transition metal was reported nearly 30 years ago,[1] the synthesis and study of such complexes have received limited investigation.[2] This may be due, in part, to the paucity of trifluoromethylating reagents available. While the synthetic chemist may choose among Grignard reagents, methyllithium, dimethylzinc, or other common alkylating agents, trifluoromethyl analogues of these standard reagents are either unknown or ineffective in the preparation of transition-metal compounds. Until recently, all trifluoromethyl complexes were synthesized by either decarbonylation of a trifluoroacetyl ligand or oxidative addition of trifluoromethyl iodide to a metal complex; both of these methods have severe limitations. A third approach has been reported by Morrison in which $Cd(CF_3)_2$ is used as the trifluoromethylating reagent.[3,4] The dimethoxyethane (DME) adduct of this species is stable enough to permit its isolation and storage, yet it is reactive enough to displace halides in nickel, palladium, platinum,[4] and cobalt[6] compounds, forming both mono- and bis(trifluoromethyl) complexes.

As part of our studies on gold alkyl compounds, we set out to synthesize the mono-, bis-, and tris(trifluoromethyl)gold phosphine complexes, $(CF_3)AuL$, $(CF_3)Au$-

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(1) Coffield, T. H.; Kozikowski, J.; Closson, R. D. *Abstr. 5th Int. Conf. Coord. Chem.*, London, 1959; p 126.

(2) Morrison, J. A. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 293.

(3) Krause, L. J.; Morrison, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 2995.

(4) Ontiveros, C. D.; Morrison, J. A. *Inorg. Synth.* **1986**, *24*, 55.

(5) Krause, L. J.; Morrison, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1282.

(6) Ontiveros, C. D.; Morrison, J. A. *Organometallics* **1986**, *5*, 1446.

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**Table I. $^{19}$F NMR Data**

| compound[a] | chem shift[b] | multiplicity[c] and coupling const | assignment |
|---|---|---|---|
| $(CF_3)AuPMe_3$ (**1**) | −29.7 | d, $^3J_{P-F}$ = 47 Hz | $CF_3$ |
| $(CF_3)AuPEt_3$ (**2**) | −30.2 | d, $^3J_{P-F}$ = 44 Hz | $CF_3$ |
| $(CF_3)AuPPh_3$ (**3**) | −28.7 | d, $^3J_{P-F}$ = 45 Hz | $CF_3$ |
| *cis*-$Br_2(CF_3)AuPMe_3$ (**4c**) | −18.2 | d, $^3J_{P-F}$ = 19 Hz | $CF_3$ |
| *trans*-$Br_2(CF_3)AuPMe_3$ (**4t**) | −22.6 | d, $^3J_{P-F}$ = 88 Hz | $CF_3$ |
| *cis*-$Br_2(CF_3)AuPEt_3$ (**5c**) | −16.4 | d, $^3J_{P-F}$ = 14 Hz | $CF_3$ |
| *trans*-$Br_2(CF_3)AuPEt_3$ (**5t**) | −23.2 | d, $^3J_{P-F}$ = 83 Hz | $CF_3$ |
| *trans*-$Br_2(CF_3)AuPPh_3$ (**6t**) | −18.2 | d, $^3J_{P-F}$ = 87 Hz | $CF_3$ |
| *cis*-$I_2(CF_3)AuPMe_3$ (**7c**) | −15.7 | d, $^3J_{P-F}$ = 15 Hz | $CF_3$ |
| *trans*-$I_2(CF_3)AuPMe_3$ (**7t**) | −7.9 | d, $^3J_{P-F}$ = 80 Hz | $CF_3$ |
| *cis*-$I_2(CF_3)AuPEt_3$ (**8c**) | −13.7 | d, $^3J_{P-F}$ = 11 Hz | $CF_3$ |
| *trans*-$I_2(CF_3)AuPEt_3$ (**8t**) | −8.2 | d, $^3J_{P-F}$ = 75 Hz | $CF_3$ |
| *cis*-$(CF_3)_2BrAuPMe_3$ (**9c**) | −28.9 | dq, $^3J_{P-F}$ = 79 Hz<br>$^4J_{F-F}$ = 8.1 Hz | $CF_3$(trans to $PMe_3$) |
|  | −24.7 | dq, $^3J_{P-F}$ = 16 Hz | $CF_3$(cis to $PMe_3$) |
| *trans*-$(CF_3)_2BrAuPMe_3$ (**9t**) | −26.0 | d, $^3J_{P-F}$ = 9.5 Hz | $CF_3$ |
| *cis*-$(CF_3)_2BrAuPEt_3$ (**10c**) | −29.1 | dq, $^3J_{P-F}$ = 74 Hz<br>$^4J_{F-F}$ = 8.1 Hz | $CF_3$(trans to $PEt_3$) |
|  | −23.4 | dq, $^3J_{P-F}$ = 12 Hz | $CF_3$(cis to $PEt_3$) |
| *trans*-$(CF_3)_2BrAuPEt_3$ (**10t**) | −24.5 | d, $^3J_{P-F}$ = 5.2 Hz | $CF_3$ |
| *cis*-$(CF_3)_2IAuPMe_3$ (**11c**) | −22.2 | dq, $^3J_{P-F}$ = 79 Hz<br>$^4J_{F-F}$ = 8.1 Hz | $CF_3$(trans to $PMe_3$) |
|  | −26.3 | dq, $^3J_{P-F}$ = 16 Hz | $CF_3$(cis to $PMe_3$) |
| *trans*-$(CF_3)_2IAuPMe_3$ (**11t**) | −19.3 | d, $^3J_{P-F}$ = 11 Hz | $CF_3$ |
| *cis*-$(CF_3)_2IAuPEt_3$ (**12c**) | −22.3 | dq, $^3J_{P-F}$ = 73 Hz<br>$^4J_{F-F}$ = 8.6 Hz | $CF_3$(trans to $PEt_3$) |
|  | −24.9 | dq, $^3J_{P-F}$ = 11 Hz | $CF_3$(cis to $PEt_3$) |
| *trans*-$(CF_3)_2IAuPEt_3$ (**12t**) | −17.7 | d, $^3J_{P-F}$ = 6.8 Hz | $CF_3$ |
| $(CF_3)_3AuPMe_3$ (**13**) | −32.3 | ds, $^3J_{P-F}$ = 79 Hz<br>$^4J_{F-F}$ = 6.4 Hz | $CF_3$(trans to $PMe_3$) |
|  | −30.6 | dq, $^3J_{P-F}$ = 10.5 Hz | $(CF_3)_2$(cis to $PMe_3$) |

[a] All spectra run in $CH_2Cl_2$. [b] All chemical shift values in ppm are upfield of $CFCl_3$. [c] Abbreviations: d, doublet; dq, doublet of quartets; ds, doublet of septets.

$(L)X_2$, $(CF_3)_2Au(L)X$, $(CF_3)_3AuL$, and investigate the physical and chemical properties of these new compounds vis-à-vis their methyl analogues. We have utilized a variety of phosphine ligands (L) in this work to examine the effect of the ligand on the reaction products. A prior investigation of (trifluoromethyl)gold chemistry appeared in a 1976 paper by Puddephatt[7] in which $CF_3I$ was used as the trifluoromethylating reagent in reactions with MeAuL. A recent communication[8] describes the preparation of $(CF_3)_3Au(PMe_3)$ via the cocondensation of gold atoms and trifluoromethyl radicals.

## Results and Discussion

**Synthesis of $(CF_3)AuL$.** Puddephatt[7] reported that trifluoromethyl iodide reacts with MeAuL in a ligand selective manner to form either $(CF_3)AuL$ (when L = $PPh_3$, $PPh_2Me$) or $(CF_3)AuMe_2(L)$ (when L = $PMe_3$, $PMe_2Ph$). We have found that a more general procedure for the preparation of $(CF_3)AuL$ compounds involves treatment of the phosphine halide complex with $(CF_3)_2Cd·DME$ in methylene chloride (eq 1).[9] Product yields are typically in the 65–75% range. These white crystalline compounds are air and moisture stable like their methyl analogues. In contrast to the alkyls, however, they are photochemically insensitive and showed no detectable change after storage for weeks in the light at room temperature. The $^{19}$F NMR spectra (Table I) of these compounds are quite characteristic: All three complexes exhibit doublets ~30 ppm upfield of $CFCl_3$ with phosphorus–fluorine coupling constants of approximately 45 Hz. These spectral results are in good agreement with those of Puddephatt[7] for his $(CF_3)AuL$ compounds. The $^1$H NMR spectrum of **1** is set out in Table II; note that the phosphine protons in **1** fall slightly upfield of those in the gold(I) halides.

$$2ClAuL + (CF_3)_2Cd{\cdot}DME \xrightarrow[CH_2Cl_2]{} 2(CF_3)AuL + CdCl_2 \qquad (1)$$

**1**: L = $PMe_3$
**2**: L = $PEt_3$
**3**: L = $PPh_3$

**Table II. $^1$H NMR Data**

| compound[a] | chem shift,[b] ppm | $^2J_{P-H}$, Hz | $^5J_{F-H}$,[b] Hz |
|---|---|---|---|
| $ClAuPMe_3$[c] | 1.61 | 11.2 |  |
| $BrAuPMe_3$[c] | 1.61 | 11.3 |  |
| $IAuPMe_3$[c] | 1.59 | 11.1 |  |
| $(CF_3)AuPMe_3$ (**1**) | 1.50 | 10.3 | *d* |
| $Br_3AuPMe_3$ | 2.14 | 13.5 |  |
| $I_3AuPMe_3$ | 2.30 | 13.4 |  |
| *cis*-$Br_2(CF_3)AuPMe_3$ (**4c**) | 2.05 | 13.2 | 0.44 |
| *trans*-$Br_2(CF_3)AuPMe_3$ (**4t**) | 1.86 | 13.1 | 0.72 |
| *cis*-$I_2(CF_3)AuPMe_3$ (**7c**) | 2.04 | 13.2 | *d* |
| *trans*-$I_2(CF_3)AuPMe_3$ (**7t**) | 2.17 | 12.5 | 0.64 |
| *cis*-$(CF_3)_2BrAuPMe_3$ (**9c**) | 1.84 | 12.6 | 0.59 |
| *cis*-$(CF_3)_2IAuPMe_3$ (**11c**) | 1.95 | 12.4 | *d* |
| $(CF_3)_3AuPMe_3$ (**13**) | 1.78 | 12.6 | *d* |

[a] All spectra run in $CH_2Cl_2$. [b] All resonances appear as 1:1 doublets; some complexes show additional quartet fine structure, denoted as $^5J_{F-H}$. [c] From ref 25. [d] Not resolved.

These new (trifluoromethyl)gold species are unlike their methyl analogues in reactions with halogens. Thus, we observe cleavage of the gold–carbon bond and evolution of methyl bromide when methylene chloride solutions of $MeAuPMe_3$ are treated with bromine; no gold alkyls are detected in the $^1$H NMR. Similar results have been obtained by Kochi[10] and Nesmeyanov[11] for $MeAuPPh_3$ and $PhAuPPh_3$, respectively. In contrast, $(CF_3)AuL$ cleanly adds excess halogen to form $(CF_3)AuX_2(L)$ in 80% isolated yields (eq 2). In this respect the trifluoromethyl species

$$(CF_3)AuL + X_2(\text{excess}) \xrightarrow[CH_2Cl_2]{} (CF_3)AuX_2(L) \qquad (2)$$

**4**: X = Br; L = $PMe_3$
**5**: X = Br; L = $PEt_3$
**6**: X = Br; L = $PPh_3$
**7**: X = I; L = $PMe_3$
**8**: X = I; L = $PEt_3$

act like the (pentahaloaryl)gold(I) complexes extensively studied by Uson.[12–15] These $(C_6X'_5)AuL$ compounds commonly add halogens to form the trans dihalides $(C_6X'_5)AuX_2L$. Comparisons of the new $(CF_3)AuX_2L$ with their methyl analogues is not possible; indeed, simple monoalkylgold(III) complexes are unknown. The yellow-

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[7] Johnson, A.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1976**, 1360.

[8] Guerra, M. A.; Bierschenk, T. R.; Lagow, R. J. *J. Organomet. Chem.* **1986**, *307*, C58.

[9] $Hg(CF_3)_2$ was ineffective as a trifluoromethylating reagent, even at 150 °C.

[10] Komiya, S.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1977**, *16*, 1253.

[11] Nesmeyanov, A. N.; Perevalova, E. G.; Grandberg, K. I.; Lemenovskii, D. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 1124.

[12] Uson, R.; Laguna, A.; Vicente, J. *Synth. React. Inorg. Met.-Org. Chem.* **1976**, *6*, 295.

[13] Uson, R.; Laguna, A.; Vicente, J. *Synth. React. Inorg. Met.-Org. Chem.* **1977**, *7*, 463.

[14] Uson, R.; Laguna, A.; Vicente, J.; Garcia, J.; Bergareche, B.; Brun, P. *Inorg. Chim. Acta* **1978**, *28*, 237.

[15] Uson, R.; Laguna, A.; Bergareche, B. *J. Organomet. Chem.* **1980**, *184*, 411.

orange dibromides and chocolate-brown diiodides are air and moisture stable. The square-planar stereochemistry of the dihalides is predominantly trans although small amounts (~3–5%) of the cis isomer are also present in all cases except $(CF_3)AuX_2(PPh_3)$. As shown in Table I, phosphorus–fluorine coupling constants are helpful in isomer identification since the trans isomers (**4t–8t**) are in the 75–90 Hz range while the cis isomers (**4c**, **5c**, **7c**, and **8c**) have much smaller couplings (10–20 Hz). This same trend was found in the $^{19}F$ spectra of *cis*- and *trans*-$(CF_3)AuMe_2(PMe_3)$ with $^3J_{P-F}$ = 11 and 66 Hz, respectively.[7] The $^{19}F$ chemical shifts of the dihalide species **4–8** are substantially downfield of their gold(I) precursors **1–3**. As shown in the $^1H$ spectra (Table II), a large downfield shift also obtains in the methyl (phosphine) resonances in the $(CF_3)AuPMe_3$ to $(CF_3)AuX_2(PMe_3)$ conversion. This is similar in direction and magnitude to the changes in the $XAu(PMe_3)/X_3Au(PMe_3)$ series.

Additional products are found when the reaction described in eq 2 is carried out with equimolar amounts of gold and halogen (eq 3). It thus appears as though unreacted $(CF_3)AuL$ undergoes rapid trifluoromethyl for halogen ligand exchange with some newly formed $(CF_3)AuX_2(L)$ (eq 4). In support of this assertion, we find that

$$(CF_3)AuL + X_2 \xrightarrow[CH_2Cl_2]{} (1-2n)(CF_3)AuX_2(L) + n(CF_3)_2AuX(L) + nAuX_3(L) \quad (3)$$

**9**: X = Br; L = PMe$_3$
**10**: X = Br; L = PEt$_3$
**11**: X = I; L = PMe$_3$
**12**: X= I; L = PEt$_3$

$$(CF_3)AuL + (CF_3)AuX_2(L) \rightarrow (CF_3)_2AuX(L) + AuX(L) \quad (4)$$

halogen-free solutions of $(CF_3)AuL$ and $(CF_3)AuX_2(L)$ do in fact combine according to eq 4 for L = $PMe_3$ or $PEt_3$. The use of a large excess of halogen (eq 2) apparently consumes all the $CF_3AuL$ before the exchange reaction (eq 4) can take place. Earlier studies have demonstrated that methyl for halogen exchange occurs between $Me_2AuI(L)$ and MeAuL[16,17] as well as between $MeAu(CF_3)I(L)$ and MeAuL.[7] Equation 4 is an extension of this type of reaction to include the trifluoromethyl ligand. We defer a discussion of the new $(CF_3)_2AuX(L)$ complexes to the next section.

Finally, when L = $PPh_3$, the reaction course is insensitive to the quantity of halogen added to $(CF_3)AuL$: The only product is $(CF_3)AuX_2(PPh_3)$, and no evidence is found for products of trifluoromethyl/halogen exchange in reactions 3 and 4. Similar behavior was observed[7] in the reaction of $CF_3I$ with MeAuL wherein methyl for iodine exchange was noted for L = $PMe_3$ and $PMe_2Ph$ but not $PPh_3$.

**Synthesis of $(CF_3)_2AuX(L)$.** Although the addition of equimolar halogen to $(CF_3)AuL$ described in the previous section results in the formation of $(CF_3)_2AuX(L)$, the maximum yield we obtained (based on $(CF_3)AuL$) was 35%; therefore, we sought other methods to obtain higher yields. Our first attempts to prepare a bis(trifluoromethyl)gold complex utilized the cadmium reagent[9] and gold(III) precursors but resulted in reduction to $(CF_3)AuL$. Sources of gold(III) included $(CF_3)AuX_2(L)$ (eq 5), $Cl_3AuPEt_3$ (eq 6), $I_3AuPPh_3$ (eq 7), and several mixed trihalides (eq 8).[18]

$$2(CF_3)AuX_2(L) + Cd(CF_3)_2{\cdot}DME \xrightarrow[CH_2Cl_2]{} 2(CF_3)AuL + 2CF_3X + CdX_2 \quad (5)$$

$$Cl_3AuPEt_3 + Cd(CF_3)_2{\cdot}DME \xrightarrow[CH_2Cl_2]{} (CF_3)AuPEt_3 + CdCl_2 + CF_3Cl \quad (6)$$

$$I_3AuPPh_3 + Cd(CF_3)_2{\cdot}DME \xrightarrow[CH_2Cl_2]{} (CF_3)AuPPh_3 + CdI_2 + CF_3I \quad (7)$$

$$3ClX_2AuL + 3Cd(CF_3)_2{\cdot}DME \xrightarrow[CH_2Cl_2]{} 3(CF_3)AuL + CdCl_2 + 2CdX_2 + 2CF_3X + CF_3Cl \quad (8)$$

L = $PMe_3$, $PEt_3$, $PPh_3$
X = Br, I

Puddephatt[7] reported the (irreproducible) preparation of $(CF_3)MeAuI(PMe_3)$ from the cis oxidative addition of trifluoromethyl iodide to $MeAuPMe_3$. We have extended this approach and find that methylene chloride solutions of $(CF_3)AuL$ react with trifluoromethyl iodide at 50 °C to generate $(CF_3)_2AuI(L)$ in 80% yield (eq 9). The rate of

$$CF_3AuL + CF_3I \xrightarrow[CH_2Cl_2]{50\ °C} (CF_3)_2AuI(L) \quad (9)$$

**11**: L = PMe$_3$
**12**: L = PEt$_3$

addition is strongly dependent on the nature of the phosphine ligand. Thus, the ratio of the disappearance half-lives for $(CF_3)AuL$ was found to be $t_{1/2}(PMe_3)/t_{1/2}(PEt_3)$ = 600. As another example of ligand effects, no reaction at all was observed with L = $PPh_3$. All attempts to prepare bromide analogues of $(CF_3)_2AuI(L)$ by using $CF_3Br$ in place of $CF_3I$ met with failure. Likewise, **1** was inert toward methyl iodide although its alkyl analogue, $MeAuPMe_3$, readily adds $CH_3I$ to form $Me_2AuI(PMe_3)$ as a primary product.[16,17]

Since $CF_3I$ takes part in many free radical reactions, we investigated the possibility of free radical involvement in eq 9 by the use of the radical scavenger galvinoxyl. Thus, methylene chloride solutions of **1** were added to two NMR tubes, one of which was spiked with galvinoxyl. Trifluoromethyl iodide was condensed into each solution and the reaction monitored by $^{19}F$ NMR. The solution without the radical scavenger rapidly formed **11** but the galvinoxyl-containing solution showed no reaction, even after several hours (during which time the other reaction went to completion). This result suggests a radical chain mechanism for the trifluoromethyl iodide addition (eq 10 and 11). Our findings are similar to those of Puddephatt[7] where free radicals were implicated in the reaction of $CF_3I$ with $MeAu(PMe_3)$.

$$^{\bullet}CF_3 + (CF_3)AuL \rightarrow [(CF_3)_2AuL]^{\bullet} \quad (10)$$

$$[(CF_3)_2AuL]^{\bullet} + CF_3I \rightarrow (CF_3)_2AuI(L) + {}^{\bullet}CF_3 \quad (11)$$

We will discuss the characterization of both the bromide and iodide in this section although the former may only be prepared by the trifluoromethyl for bromine exchange mentioned in the previous section. All of the pale yellow $(CF_3)_2AuX(L)$ compounds are air and moisture stable. The $^{19}F$ NMR spectra of these complexes are set out in Table I, and a representative example is shown in Figure 1. Although the cis isomer predominates (~95%), the presence of both cis and trans isomers is in contrast to the analogous $Me_2AuX(L)$ complexes in which only the cis

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[16] Johnson, A.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *85*, 115.

[17] Tamaki, A.; Kochi, J. K. *J. Organomet. Chem.* **1974**, *64*, 411.

[18] Although we have represented the "mixed trihalides" as $ClX_2AuL$, it is likely that a mixture of all six isomers of the type $AuCl_nX_{3-n}(L)$ ($n$ = 0–3), exists in solution.[19]

[19] Heaton, B. T.; Kelsey, R. J. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 363.

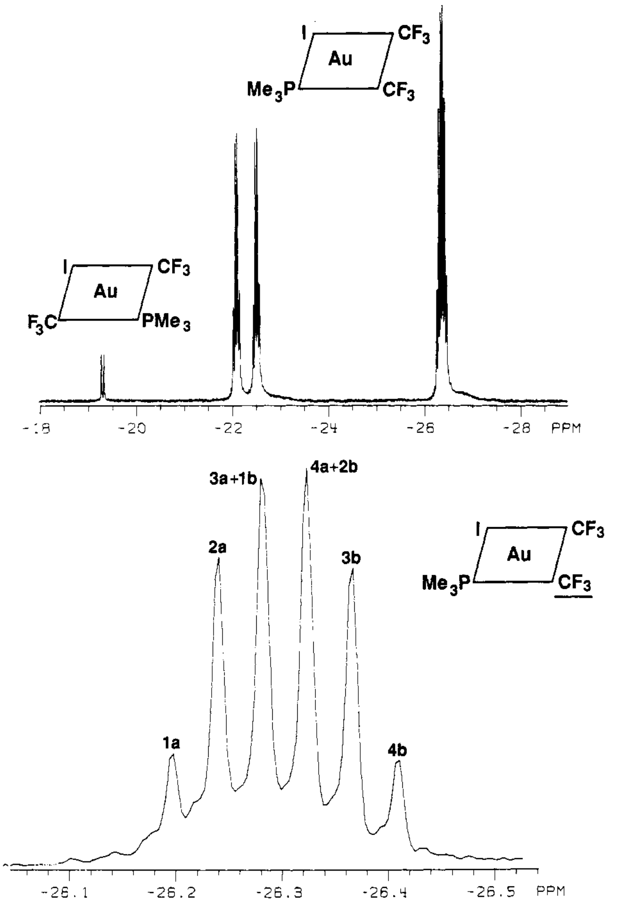

**Figure 1.** $^{19}F$ NMR spectrum ($CH_2Cl_2$, 188.25 MHz, $CFCl_3$ reference) of $(CF_3)_2AuI(PMe_3)$.

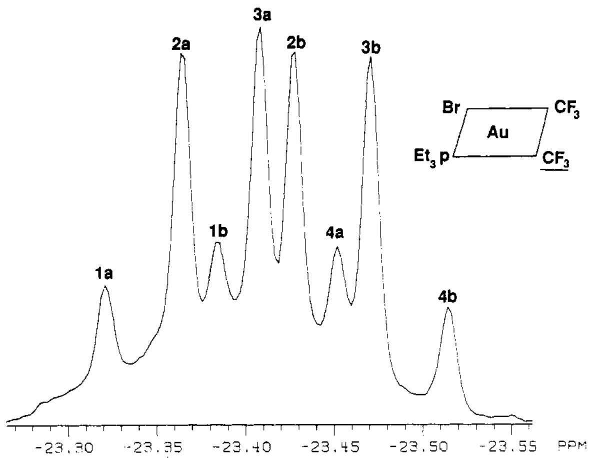

**Figure 2.** $^{19}F$ NMR spectrum ($CH_2Cl_2$, 188.25 MHz, $CFCl_3$ reference) of $(CF_3)_2AuBr(PEt_3)$.

isomer is found.[20,21] The isomers of $(CF_3)_2AuX(L)$ are easily distinguished on the basis of their splitting patterns. Figure 1 (top) shows the expected doublet ($^3J_{P-F}$ = 11 Hz) at −19.3 ppm for the equivalent trifluoromethyl ligands in **11t**. The small value of $^3J_{P-F}$ is in accord with both $CF_3$ ligands oriented cis to the trimethylphosphine (cf. cis-$(CF_3)AuX_2(L)$ in Table I).

Each $CF_3$ group in cis-$(CF_3)_2AuX(L)$ should, to first order, appear as a doublet ($^3J_{P-F}$) of quartets ($^4J_{F-F}$) with a substantially larger phosphorus–fluorine coupling for the $CF_3$ group trans to the phosphine. (Recall $^3J_{P-F} \sim$ 75–90 Hz for *trans*-$(CF_3)AuX_2(L)$ and 10–20 Hz for *cis*-$(CF_3)$-$AuX_2(L)$.) Indeed, Figure 1 (top) shows a well-separated doublet of quartets at −22.2 ppm with $^3J_{P-F}$ = 79 Hz and $^4J_{F-F}$ = 8.1 Hz which we assign to the $CF_3$ ligand trans to trimethylphosphine in **11c**. Although there are no other bis(trifluoromethyl) compounds with inequivalent $CF_3$ groups available for comparison, $^4J_{F-F}$ = 4.9 Hz in $Hg(CF_3)_2$ (measured from $^{13}C$ satellites).[22] Two (trifluoromethyl)selenium compounds, $(CF_3)SeCF_2Cl$ and $(CF_3)SeCFCl_2$, have $^4J_{F-F}$ values of 7.5 and 7.0 Hz, respectively.[23,24] Finally, Figure 1 (bottom) shows a complex pattern which may be fit to an (exactly) overlapping doublet of quartets (denoted in the figure as quartets "a" and "b"), with $^3J_{P-F}$ = 16 Hz and $^4J_{F-F}$ = 8.1 Hz, at a chemical shift of −26.3 ppm. We assign this spectral feature to the trifluoromethyl group cis to $PMe_3$ in **11c** based on the small phosphorus–fluorine coupling. The exact overlap of quartets seen here is due to the fortuitous relationship of the coupling constants in this complex: $^3J_{P-F} = 2(^4J_{F-F})$. Saturation of the resonance at −22.2 ppm in a homonuclear decoupling experiment eliminates the fluorine–fluorine coupling and causes the resonance at −26.3 ppm to collapse to a simple doublet with $^3J_{P-F}$ = 16 Hz. Figure 2 shows the nicely separated pattern found for the triethylphosphine analogue **10c** in which the overlapping "a" and "b" quartets are readily apparent since, in this complex, $^3J_{P-F} \neq 2(^4J_{F-F})$.

**Relationship of NMR Chemical Shifts to Structure.** Earlier work by Goodfellow and co-workers has examined the effect of stereochemistry on proton chemical shifts of trimethylphosphine, trimethylarsine, and dimethyl sulfide ligands in square-planar platinum and palladium complexes.[25-28] It was found that changes in the halide trans to the neutral ligand had little impact while $^1H$ chemical shifts for the complexes with a halide in the cis position fell in the order $\delta(I) > \delta(Br) > \delta(Cl)$. Further, the magnitude of the chemical shift difference depended on both the identity *and* number of cis halides. These authors ascribed this behavior to the through-space effects of (1) the electric dipole of the M–X bond and (2) the induced magnetic dipole due to the magnetic anisotropy of the M–X bond.[29]

We have seen similar effects on the proton chemical shift of the trimethylphosphine ligand for our square-planar gold(III) complexes. Reference to the last column of Table III shows a downfield shift of 0.31 ppm occurs when two cis (to the phosphine) bromides are changed to iodides in *trans*-$X_2(CF_3)AuPMe_3$; the proximity of only one cis halide in *cis*-$(CF_3)_2XAuPMe_3$ reduces this shift to 0.11 ppm. Our data suggest that a trans halide has the opposite effect: an *upfield* shift of 0.02 ppm is found for *cis*-$X_2(CF_3)$-$AuPMe_3$ in which the stereochemistry indicates one cis halide and one trans halide. The magnitude of the upfield shift due to the trans halide can be estimated if we assume that the cis halide causes a downfield shift of 0.11 ppm (as found in *cis*-$(CF_3)_2XAuPMe_3$). An upfield contribution

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**Table III. Halide-Induced Chemical Shift Differences**

| compound | square-planar ligand geometry | $\delta$(I) − $\delta$(Br),[a] ppm | | |
|---|---|---|---|---|
| | | $^{19}$F | | $^{1}$H |
| | | L = $PMe_3$ | L = $PEt_3$ | L = $PMe_3$ |
| *trans*-$X_2(CF_3)AuL$ | $CF_3$, L cis to 2X | 14.7 | 15.0 | 0.31 |
| *cis*-$(CF_3)_2XAuL$ | $CF_3$, L cis to 1X | 6.7 | 6.8 | 0.11 |
| *trans*-$(CF_3)_2XAuL$ | $CF_3$ cis to 1X | 6.7 | 6.8 | |
| *cis*-$X_2(CF_3)AuL$ | $CF_3$, L cis to 1X, trans to 1X | 2.5 | 2.7 | −0.02 |
| *cis*-$(CF_3)_2XAuL$ | $CF_3$ trans to 1X | −1.6 | −1.5 | |
| $X_3AuL$ | L cis to 2X, trans to 1X | | | 0.16 |

[a] This is the $^{19}$F or $^{1}$H chemical shift difference upon Br → I substitution; a positive value indicates a downfield shift.

of 0.13 ppm would then be required to yield the resultant −0.02 ppm shift. Another example of the upfield effect of the trans halide is provided by $X_3AuPMe_3$. If we make the approximation that the two cis (to the phosphine) halides in this complex lead to a downfield shift of 0.31 ppm (as in *trans*-$X_2(CF_3)AuPMe_3$), then an upfield shift of 0.15 ppm due to the trans halide would provide the observed 0.16 ppm difference. Although these approximations will certainly not furnish the exact magnitude of the trans induced shift, we do feel that an upfield direction is indicated.

A far more compelling argument for halide-induced NMR shifts is supplied by our $^{19}$F results. In these examples, then, we are focusing on the trifluoromethyl ligand and present data for both trimethyl- and triethylphosphine complexes. One remarkable feature of Table III is the nearly identical results displayed by the two series of compounds containing different phosphines. Furthermore, trends exhibited by the $^{19}$F nucleus are the same as those previously discussed for $^{1}$H NMR: Downfield shifts of $^{19}$F resonances upon substitution of iodide for bromide are found for structures with halide(s) cis to $CF_3$. This effect is especially pronounced for the doubly cis complexes *trans*-$X_2(CF_3)AuL$. The compounds having trifluoromethyl group(s) singly cis to a halide (for example, *trans*-$(CF_3)_2XAuL$) exhibit shifts that are approximately one-half those of the doubly cis compounds. A contribution from an upfield shift caused by a trans halide is suggested by the small value (compared to, for example, *trans*-$(CF_3)_2XAuL$) found for the downfield shift in *cis*-$X_2(CF_3)AuL$, which has one cis and one trans halide. This is the same sort of argument we used to propose an upfield shift component due to a trans halide in the $^{1}$H spectra. In the $^{19}$F spectra, however, an unambiguous test of this assertion is furnished by the $CF_3$ ligand trans to the halide in *cis*-$(CF_3)_2XAuL$: upfield shifts, as proposed, are found in these complexes.

**Synthesis of $(CF_3)_3AuPMe_3$.** In an attempt to extend the halogen/trifluoromethyl exchange reaction beyond the scope represented by eq 4, we combined complexes 1 and 11 in boiling methylene chloride. Even though the analogous procedure[16] with $MeAuPMe_3$ and *cis*-$Me_2AuI(PMe_3)$ yields $Me_3AuPMe_3$, our trifluoromethylated species showed no reaction after 12 h. Another approach to the synthesis of the fully trifluoromethylated gold(III) complex **13** utilized the cadmium reagent. As shown in eq 12, this route

$$\underset{\mathbf{11}}{3(CF_3)_2AuI(PMe_3)} + Cd(CF_3)_2{\cdot}DME \xrightarrow[CH_2Cl_2]{} \underset{\mathbf{13}}{2(CF_3)_3AuPMe_3} + \underset{\mathbf{1}}{CF_3AuPMe_3} + CF_3I + CdI_2 \quad (12)$$

did produce the target molecule but was plagued by the reductive elimination of trifluoromethyl iodide with concomitant formation of **1**. (No reduction is observed[30] when the methyl analog, $Me_2AuCl(PMe_3)$, is treated with methyllithium.) We found it possible to inhibit this elimination reaction by carrying out the synthesis under a trifluoromethyl iodide atmosphere. This method led to an 80% yield of the fully trifluoromethylated product (eq 13).

$$\underset{\mathbf{11}}{2(CF_3)_2AuI(PMe_3)} + Cd(CF_3)_2{\cdot}DME \xrightarrow[CH_2Cl_2]{CF_3I} \underset{\mathbf{13}}{2(CF_3)_3AuPMe_3} + CdI_2 \quad (13)$$

The white crystalline compound **13** is air and moisture stable; unlike its methyl analogue, it may be stored for weeks at room temperature without appreciable decomposition and methylene chloride solutions of the complex remain unchanged for several days. The $^{19}$F NMR spectrum (Table I and Figure 3) is entirely in accord with a square-planar structure having two inequivalent sets of trifluoromethyl ligands. Figure 3 (top) gives an overview spectrum which clearly shows the two sets of resonances in the expected 2:1 intensity ratio. The $CF_3$ group trans to the phosphine should, to first order, appear as a well-separated doublet ($^{3}J_{P-F}$) of septets ($^{4}J_{F-F}$); Figure 3 (middle) exhibits just such a pattern (intensity ratio within the septet is 1:6:15:20:15:6:1), with $^{3}J_{P-F}$ = 79 Hz and $^{4}J_{F-F}$ = 6.4 Hz at a chemical shift of −32.3 ppm. These coupling constants are very close to those found for the trans trifluoromethyl group in **9c** and **11c**. The two equivalent $CF_3$ groups cis to the phosphine in **13** should appear as a doublet of quartets which, if the results for **9c** and **11c** serve as an accurate guide, might be expected to overlap severely. Figure 3 (bottom) shows a closeup of this spectral feature with the "a" and "b" quartets labeled to aid in identification; $^{3}J_{P-F}$ = 10.5 Hz compared to 16 Hz in *cis*-$(CF_3)_2AuX(PMe_3)$. (In a homonuclear decoupling experiment similar to that described above for **11c**, saturation of the resonance at −32.3 ppm caused the overlapping doublet of quartets at −30.6 ppm to collapse to a doublet with $^{3}J_{P-F}$ = 10 Hz.) The upfield chemical shifts displayed by **13** are the largest we measured for the (trifluoromethyl)gold complexes described in this paper. Reference to Table I reveals a clear trend of increased shielding with increased trifluoromethyl coordination. This trend is reflected in the $^{1}$H NMR spectra of the trimethylphosphine ligand (Table II) wherein $I_3AuPMe_3$ (2.30 ppm) and $(CF_3)_3AuPMe_3$ (1.78 ppm) represent the two extremes of this Au(III) series.

A final word is in order concerning the recently reported preparation of **13** by the cocondensation of gold atoms and trifluoromethyl radicals.[8] If we assume that the $^{19}$F NMR chemical shifts reported by these authors as downfield from $CFCl_3$ are in fact *upfield*, then our results are nearly identical with theirs, suggesting that both groups have prepared the same compound. We seem to see a bit more structure in our $^{19}$F spectrum, however. Thus, they report that the two equivalent $CF_3$ groups cis to $PMe_3$ appear as

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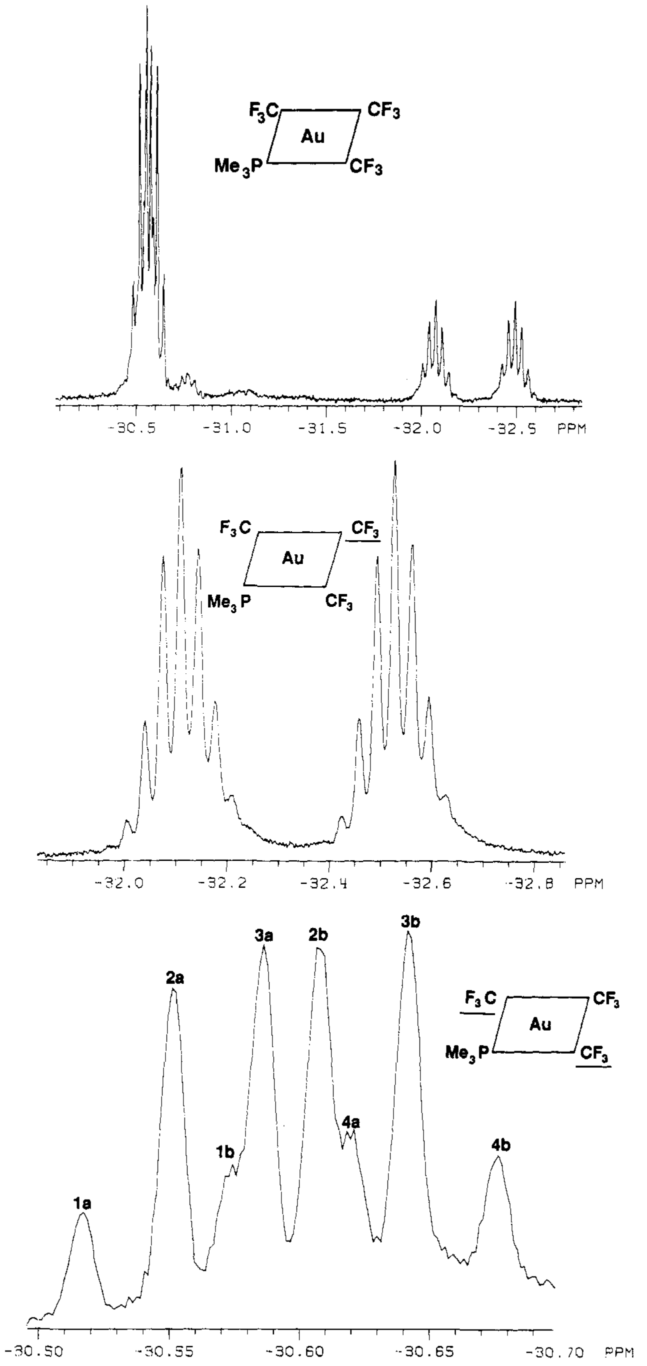


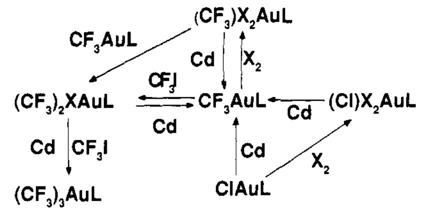
**Figure 3.** $^{19}$F NMR spectrum ($CH_2Cl_2$, 188.25 MHz, $CFCl_3$ reference) of $(CF_3)_3Au(PMe_3)$.

a singlet while we see a doublet of quartets; their trans $CF_3$ resonance is a doublet while our spectrum reveals a doublet of septets, although the doublet splitting ($^3J_{P-F}$) in both reports is near 80 Hz. Finally, the two studies show a similar chemical shift for the $PMe_3$ group of **13** in the $^1$H NMR but the earlier study noted $^2J_{P-H}$ = 5.6 Hz while we measure 12.6 Hz, a value near what is generally found in square-planar gold complexes.[21]

## Conclusion

We have prepared the (trifluoromethyl)gold(I) phosphine compounds $(CF_3)AuL$ and the entire series of gold(III) complexes $(CF_3)_nAuX_{3-n}(L)$ ($n$ = 1-3). An overview of these reactions is presented in Scheme I. The cadmium reagent $Cd(CF_3)_2$·DME, while quite suitable in some instances, does not have the general applicability of a Grignard or lithium reagent. In particular, we found that it promotes the reduction of Au(III) in cases where methyllithium is known to act as a suitable substitution reagent.[17,30,31] However, its use here as a trifluoromethylating reagent for Au(I) and, under certain conditions, for Au(III) extends its scope beyond the previous confines of the group VIII metals and suggests its inclusion in the short list of procedures available to synthesize transition-metal trifluoromethyl complexes.

Scheme I



L = $PMe_3$, $PEt_3$, $PPh_3$
Cd = $Cd(CF_3)_2$·DME
X = Br, I

## Experimental Section

**General Considerations.** Some manipulations, as noted, were performed under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a high vacuum line (Hg diffusion pump). Dimethoxyethane was purified by vacuum transfer from benzophenone ketyl. Methylene chloride was washed with concentrated sulfuric acid and then with aqueous carbonate and water, followed by drying over calcium chloride; the solvent was then distilled from $P_2O_5$ and vacuum transferred from 4-Å molecular sieves. Diethyl ether was vacuum transferred first from $LiAlH_4$ and then from titanocene.[32] Petroleum ether (30–60 °C) was vacuum transferred from 4-Å molecular sieves and then from titanocene. Methanol was distilled from 4-Å molecular sieves. Argon was purified by passing over 4-Å molecular sieves and MnO on vermiculite.[33] Trifluoromethyl iodide (PCR) was freeze–pump–thawed three times prior to use. Chlorine (Matheson) was used without purification. Iodine (Mallinckrodt) was sublimed in vacuo prior to use and bromine (Mallinckrodt AR) was used as received. Methyl iodide (Aldrich Gold Label) was passed through a column of activated alumina, distilled, and vacuum transferred from 4-Å molecular sieves contained in a foil-wrapped flask. $ClAuPMe_3$ (Johnson Matthey) and $ClAuPEt_3$ (Engelhard) were recrystallized from hot ethanol; $ClAuPPh_3$ (Aldrich) was used without further purification. XAuL (X = Br, I) complexes were prepared by metathesis of ClAuL with tetraalkylammonium halides (L = $PPh_3$)[34] or potassium halides (L = $PMe_3$, $PEt_3$)[35] according to published procedures. $X_3AuL$ compounds were prepared by treatment of XAuL with the appropriate halogen;[36] mixed-halide complexes $ClX_2AuL$ were synthesized from ClAuL and halogen by literature procedures.[18,36] $Cd(CF_3)_2$·DME,[4] $Hg(CF_3)_2$,[37] and $MeAuPMe_3$[38] were prepared according to the literature.

NMR spectra were recorded on a Nicolet NT-200 spectrometer operating at 200.07 MHz ($^1$H), 188.25 MHz ($^{19}$F), or 80.99 MHz ($^{31}$P). $^1$H chemical shifts are reported in parts per million versus TMS internal standard at 0.00 ppm; $^{19}$F chemical shifts are reported versus $CFCl_3$ internal standard at 0.00 ppm with negative values upfield of the standard. $^{31}$P chemical shifts are reported in parts per million versus 85% phosphoric acid at 0.00 ppm with negative values upfield of the standard. Mass spectra were re-

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corded on a Hewlett-Packard Model 5985 GC/MS using electron-impact ionization with 70-eV electron energy; the samples were introduced directly into the mass spectrometer via a solids probe. Elemental analysis was performed by Midwest Microlab, Indianapolis, IN.

**Procedures. $CF_3AuPMe_3$ (1).** A suspension of $Cd(CF_3)_2 \cdot DME$ (0.92 g, 2.71 mmol) in 15 mL of $CH_2Cl_2$ was prepared in the glovebox. To this stirred suspension was added, dropwise, a solution of $ClAuPMe_3$ (1.40 g, 4.55 mmol) in 25 mL of $CH_2Cl_2$; a dark brown solid was immediately formed upon addition of the gold complex. The reaction mixture was stirred for 18 h in the glovebox. The suspension was then removed from the glovebox and filtered in the air, leaving a brown solid and a light tan filtrate. The solid was washed with two portions of methylene chloride, and the washings were combined with the original filtrate. This solution was placed on the vacuum line and concentrated until a saturated solution was formed. Addition of diethyl ether resulted in the formation of crystals that were collected and washed with cold ether, yielding 0.84 g of white crystalline product. The $CH_2Cl_2/Et_2O$ filtrate was cooled to -30 °C to obtain an additional 0.27 g. The overall yield was 1.11 g (3.25 mmol), 71% based on $ClAuPMe_3$. MS: *m/e* (relative intensity) 342 (1.0), parent ion; 323 (9.0), $CF_2AuPMe_3$; 273 (100), $AuPMe_3$. Anal. Calcd for $C_4H_9F_3PAu$: C, 14.05; H, 2.65; F, 16.66, P, 9.06. Found: C, 14.26; H, 2.58; F, 16.34; P, 9.47.

**$CF_3AuPEt_3$ (2).** This compound was prepared by using the same procedure as 1 except the original methylene chloride filtrate was pumped to dryness on a vacuum line and the solid was taken up in minimum $Et_2O$. Cooling this solution to -80 °C produced crystals that were washed with petroleum ether; 65% yield. $^{31}P$ $\{^1H\}$ NMR ($CH_2Cl_2$, chemical shift relative to triphenylphosphine oxide external standard at 27.0 ppm): 25.4 ppm (q, $^3J_{P-F}$ = 44 Hz, $PEt_3$). MS: *m/e* (relative intensity) 384 (0.2), parent ion; 365 (26), $CF_2AuPEt_3$; 315 (100), $AuPEt_3$. Anal. Calcd for $C_7H_{15}F_3PAu$: C, 21.89; H, 3.94; F, 14.84; P, 8.06. Found: C, 22.24; H, 4.37; F, 15.03; P, 8.27.

**$CF_3AuPPh_3$ (3).** This compound has been previously prepared by a different route.[7] Our procedure was the same as that used to prepare 1 except equimolar $ClAuPPh_3$ and $Cd(CF_3)_2 \cdot DME$ were used. The original methylene chloride filtrate was pumped to dryness on a vacuum system and the solid dissolved in boiling methanol. This solution was concentrated to a saturated condition and the product crystallized during slow cooling. Washing with cold methanol yielded 74% in two crops. Absence of $ClAuPPh_3$ starting material was verified by $^{31}P$ NMR. $^{31}P$ $\{^1H\}$ NMR for 3 ($CH_2Cl_2$, chemical shift relative to triethyl phosphite external standard at 138.0 ppm): 37.2 ppm (q, $^3J_{P-F}$ = 45 Hz, $PPh_3$). $^{31}P\{^1H\}$ NMR for $ClAuPPh_3$ (same conditions as 3): 32.2 ppm (s, $PPh_3$).

**$Hg(CF_3)_2$ and ClAuL (L = $PMe_3$, $PEt_3$, $PPh_3$).** In the glovebox, a solution of $ClAuPMe_3$ (28 mg, 0.09 mmol) and $Hg(CF_3)_2$ (60 mg 0.18 mmol) in ~1 mL of $CH_2Cl_2$ was prepared and added to an NMR tube that had previously been sealed onto a 14/20 outer ground glass joint. A Teflon needle valve fitted with a 14/20 inner glass joint was attached to this NMR tube, and the assembly was removed from the glovebox and attached to a vacuum line. The NMR tube was torch sealed under an argon atmosphere. No reaction was observed in the $^{19}F$ NMR even after 15 h at 60 °C. A similar procedure with $ClAuPPh_3$ also showed no reaction. A final attempt with $ClAuPEt_3$ used diglyme as the solvent. The NMR tube was heated for 2 h at 150 °C, but no (trifluoromethyl)gold compounds were observed in the $^{19}F$ NMR.

**$CF_3AuBr_2(PMe_3)$ (4).** To a stirred solution of bromine (0.70 g, 4.38 mmol) in 15 mL of $CH_2Cl_2$ was added $CF_3AuPMe_3$ (0.30 g, 0.88 mmol) in several small portions. The solvent was allowed to evaporate from the red-orange solution in a fume hood until 5 mL remained. Addition of diethyl ether resulted in the formation of orange-yellow crystals of 4 that were collected and washed with cold ether, yielding 0.25 g of product. The filtrate and washings were combined and cooled to -30 °C to obtain a second crop of 0.10 g. The overall yield was 0.35 g (0.70 mmol), 80% based on $CF_3AuPMe_3$. $^{31}P$ $\{^1H\}$ NMR for **4t** ($CH_2Cl_2$, chemical shift relative to triethyl phosphite external standard at 138.0 ppm): -5.6 ppm (q, $^3J$ = 88 Hz, $PMe_3$). MS: *m/e* (relative intensity) 500, 502, 504 (1.7, 3.1, 1.5), parent ion; 431, 433, 435 (0.5, 1.4, 0.5), $Br_2AuPMe_3$; 421, 423 (2.5, 2.3), $CF_3AuBr(PMe_3)$; 352, 354 (16, 16), $BrAuPMe_3$; 337, 339 (0.8, 0.8), $BrAuPMe_2$; 323 (0.6), $CF_2AuPMe_3$; 276, 278 (7.1, 6.9), AuBr; 273 (100), $AuPMe_3$. Anal. Calcd for $C_4H_9Br_2F_3PAu$: C, 9.57; H, 1.81; Br, 31.86; F, 11.36; P, 6.17. Found: C, 9.77; H, 2.06; Br, 31.37; F, 11.41; P, 5.82.

**$CF_3AuBr_2(PEt_3)$ (5).** This compound was prepared by using the same procedure as 4, 78% yield of orange crystals. MS: *m/e* (relative intensity) 473, 475, 477 (3.9, 7.1, 3.8), $Br_2AuPEt_3$; 394, 396 (7.4, 7.3), $BrAuPEt_3$; 365 (3.0), $CF_2AuPEt_3$; 315 (100), $AuPEt_3$. Anal. Calcd for $C_7H_{15}Br_2F_3PAu$: C, 15.46; H, 2.78; Br, 29.38; F, 10.48; P, 5.69. Found: C, 15.49; H, 2.71; Br, 29.91; F, 10.80; P, 5.99.

**$CF_3AuBr_2(PPh_3)$ (6).** A $CH_2Cl_2$ solution (10 mL) containing bromine (0.057 g, 0.35 mmol) was added dropwise to a $CH_2Cl_2$ solution (20 mL) of $CF_3AuPPh_3$ (0.177 g, 0.32 mmol). The resulting red-orange solution was concentrated to 5 mL, and 120 mL of petroluem ether (30–60 °C) was added, causing the formation of orange crystals of 6. After this mixture was cooled at 5 °C for 2 h, the crystals were collected and washed with petroleum ether. The yield was 0.186 g (0.26 mmol), 81% based on $CF_3AuPPh_3$. $^{31}P$ $\{^1H\}$ NMR ($CH_2Cl_2$, chemical shift relative to triphenylphosphine oxide external standard at 27.0 ppm): 22.8 ppm (q, $^3J_{P-F}$ = 87 Hz, $PPh_3$). Anal. Calcd for $C_{19}H_{15}Br_2F_3PAu$: C, 32.27; H, 2.14; Br, 22.60; F, 8.06; P, 4.38. Found: C, 32.98; H, 2.12; Br, 22.49; F, 7.43; P, 4.10.

**$CF_3AuI_2(PMe_3)$ (7).** Iodine (0.75 g, 2.95 mmol) was finely ground and added to 10 mL of $CH_2Cl_2$ in a 25-mL round-bottom flask. To this stirred solution was added $CF_3AuPMe_3$ (0.20 g, 0.58 mmol) in several small portions. After 1 h at room temperature, the solvent was removed from the dark brown solution on a vacuum line, with a liquid-nitrogen-cooled trap between the reaction mixture and the vacuum system. A dynamic vacuum was maintained overnight on the reaction flask to sublime the excess iodine into the cold trap. The product was then washed with two portions of -80 °C diethyl ether, and the solid was pumped on overnight again to remove the last traces of iodine. The chocolate brown crystals were removed from the flask the next day, yielding 0.27 g (0.45 mmol), 78% based on $CF_3AuPMe_3$. $^{31}P$ $\{^1H\}$ NMR for **7t** ($CH_2Cl_2$, chemical shift relative to triethyl phosphite external standard at 138.0 ppm): -22.7 ppm (q, $^3J_{P-F}$ = 80 Hz, $PMe_3$). MS, *m/e* (relative intensity) 596 (0.7), parent ion; 527 (4.7), $I_2AuPMe_3$; 400 (12), $IAuPMe_3$; 324 (6.5), AuI; 323 (3.5), $CF_2AuPMe_3$; 273 (100), $AuPMe_3$. Anal. Calcd for $C_4H_9F_3I_2PAu$: C, 8.06; H, 1.52; F, 9.57; I, 42.60; P, 5.20. Found: C, 8.15; H, 1.51; F, 9.78; I, 42.90; P, 5.00.

**$CF_3AuI_2(PEt_3)$ (8).** This compound was prepared on a small scale in an NMR tube reaction. $CF_3AuPEt_3$ (20 mg, 0.052 mmol) was added to a methylene chloride (1 mL) solution of iodine (60 mg, 0.24 mmol) in an NMR tube. The $^{19}F$ NMR spectrum showed **8c** and **8t** as the only fluorine-containing species. Product identification was made by comparison with the $^{19}F$ chemical shifts and coupling constants of **7c** and **7t**.

**$MeAuPMe_3$ and Halogens.** $MeAuPMe_3$ (15 mg, 0.052 mmol) was added to a solution of bromine (40 mg, 0.25 mmol) in $CH_2Cl_2$ contained in an NMR tube. The $^1H$ NMR spectrum of this reaction mixture showed $CH_3Br$ and $Br_3AuPMe_3$ as the largest resonances; no evidence for gold alkyls was found. In a similar reaction, $MeAuPMe_3$ was added to an $I_2/CH_2Cl_2$ solution. The $^1H$ NMR revealed peaks for $CH_3I$ and $I_3AuPMe_3$, but no gold alkyl species were found.

**$(CF_3)_2AuBr(PMe_3)$ (9). Method A.** A solution of bromine (0.12 g, 0.75 mmol) in 10 mL of methylene chloride was added dropwise to $CF_3AuPMe_3$ (0.25 g, 0.73 mmol) in 10 mL of methylene chloride, forming an orange solution. The solvent was removed in vacuo, and the solid residue was examined by $^1H$ and $^{19}F$ NMR; 4 (50%) and $Br_3AuPMe_3$ (25%) were identified by comparison to known spectral values. Another species (25%) was identified as **9c** by the close similarity of its splitting pattern and coupling constants to the fully characterized *cis*-$(CF_3)_2AuI(PMe_3)$. Several attempts to separate 4 and 9 in order to obtain an analytical quality sample were unsuccessful. Reactions run using several different bromine/$CF_3AuPMe_3$ ratios also failed to yield pure 9. However, mass spectra of a sample containing ~90% 9 were run. Electron-impact MS: *m/e* (relative intensity) 471, 473 (0.3, 0.3), $(CF_3)(CF_2)AuBr(PMe_3)$; 421, 423 (14, 13), $CF_3AuBr(PMe_3)$; 352, 354 (2.7, 2.7), $BrAuPMe_3$; 337, 339 (1.3, 1.9), $BrAuPMe_2$; 323 (1.4), $CF_2AuPMe_3$; 276, 278 (1.5, 1.5), AuBr; 273

(100), $AuPMe_3$. Chemical ionization MS (run using methane reagent gas with 70-eV electron energy): *m/e* (relative intensity) 471, 473 (32, 33), $(CF_3)(CF_2)AuBr(PMe_3)$; 411 (12), $(CF_3)_2AuPMe_3$; 323 (38), $CF_2AuPMe_3$; 273 (100), $AuPMe_3$.

**Method B.** $CF_3AuPMe_3$ (100 mg, 0.29 mmol) was added to a solution of $CF_3AuBr_2(PMe_3)$ (140 mg, 0.28 mmol) in 15 mL of methylene chloride. The solution color changed from orange-yellow to pale yellow immediately upon addition of the gold(I) complex. After the reaction was stirred for 1 h at room temperature, the solution was filtered to remove a suspended dark solid. The resultant light yellow filtrate was taken to dryness on a vacuum line, and the residue was extracted with two 20-mL portions of diethyl ether. Slow cooling to −80 °C yielded 95 mg of a pale yellow product. $^{19}F$ and $^1H$ NMR analysis indicated the presence of **9c** (80%), **9t** (5%), and **4** (15%); **9c** and **9t** were identified by comparison of their splitting patterns and coupling constants with the fully characterized iodo analogues, **11c** and **11t**. As in method A, we were unable to obtain **9** in sufficient purity for elemental analysis.

**$(CF_3)_2AuBr(PEt_3)$ (10). Method A.** In an NMR tube reaction, **10** was prepared as in **9**, method A. $CF_3AuPEt_3$ (20 mg, 0.052 mmol) and $Br_2$ (7 mg, 0.044 mmol) were combined in 0.5 mL of $CH_2Cl_2$. An $^{19}F$ NMR spectrum run after 2 h showed **5t**, **10c** (major product), and **10t**. The isomers of **10** were identified by the close similarity of their $^{19}F$ spectra to **9c** and **9t**.

**Method B.** In an NMR tube reaction, $CF_3AuBr_2(PEt_3)$ (20 mg, 0.037 mmol) and $CF_3AuPEt_3$ (14 mg, 0.036 mmol) were combined in 1 mL of $CH_2Cl_2$. The orange solution slowly changed to light yellow, and after 1 h, **10c** (97%) and **10t** (3%) were identified by the close similarity of their $^{19}F$ NMR spectra to **9c** and **9t**.

**$CF_3AuPPh_3$ and $CF_3AuBr_2(PPh_3)$.** This NMR tube reaction was carried out as in **9**, method B. No reaction was observed in the $^{19}F$ NMR after 1 day at room temperature.

**$(CF_3)_2AuI(PMe_3)$ (11). Method A.** A solution of $CF_3AuPMe_3$ (0.30 g, 0.87 mmol) in 15 mL of $CH_2Cl_2$ was syringed into a 25-mL cylindrical heavy-walled glass reaction vessel that had a Teflon needle valve and ground glass joint sealed onto one end. This solution was freeze–pump–thaw degassed on a vacuum line. $CF_3I$ (3.0 mmol) was measured into a calibrated volume on the vacuum line and frozen into the reaction flask with liquid nitrogen. The Teflon needle valve was closed, and the reaction vessel was heated overnight at 50 °C during which time the solution changed from colorless to light yellow. The solvent was removed in vacuo, and the solid residue was extracted with several portions of warm diethyl ether. These extracts were combined and slowly cooled to −80 °C during which time pale yellow crystals of **11** precipitated. The product was collected, washed with ice-cold ether, and air-dried to yield 0.39 g (0.72 mmol), 83% based on $CF_3AuPMe_3$. The $^{19}F$ NMR spectrum showed **11c** (97%) and **11t** (3%). MS: *m/e* (relative intensity): 538 (3.9), parent ion; 519 (0.3), $(CF_3)(CF_2)AuI(PMe_3)$; 469 (11), $CF_3AuI(PMe_3)$; 411 (6.3), $(CF_3)_2AuPMe_3$; 400 (9.1), $IAuPMe_3$; 374 (2.6), $CF_2AuI$; 324 (8.6), AuI; 323 (2.1), $CF_2AuPMe_3$; 273 (100), $AuPMe_3$. Anal. Calcd for $C_5H_9F_6IPAu$: C, 11.16; H, 1.69; F, 21.19; I, 23.59; P, 5.76. Found: C, 11.24; H, 1.51; F, 21.70; I, 23.98; P, 5.88.

**Method A with Galvinoxyl.** In parallel NMR tube experiments, $CF_3AuPMe_3$ (30 mg, $8.7 \times 10^{-2}$ mmol) was added to each of two NMR tubes that had previously been sealed to ground glass joints. Galvinoxyl ($4.7 \times 10^{-4}$ mmol) was added to one of the tubes, and 0.5 mL of $CH_2Cl_2$ was distilled into each tube on a vacuum line. $CF_3I$ (0.30 mmol) was frozen into each tube from a calibrated volume, and the tubes were flame sealed under vacuum with the reaction mixtures still frozen. The solutions were heated 5 h at 50 °C during which time the galvinoxyl-containing solution retained its intense purple color. $^{19}F$ NMR analysis showed no reaction in the galvinoxyl-spiked sample; the tube without galvinoxyl showed complete conversion to **11**.

**Method B.** In an NMR tube reaction, $CF_3AuI_2(PMe_3)$ (25 mg, 0.042 mmol) and $CF_3AuPMe_3$ (14 mg, 0.041 mmol) were combined in 0.5 mL of $CH_2Cl_2$. The brown solution slowly changed to pale yellow; after 3 h, $IAuPMe_3$ and **11c** were identified by $^1H$ and $^{19}F$ NMR.

**Method C.** In an NMR tube reaction, $CF_3AuPMe_3$ (20 mg, 0.058 mmol) and $I_2$ (15 mg, 0.059 mmol) were combined in 0.5 mL of $CH_2Cl_2$. $^{19}F$ and $^1H$ NMR spectra run after 2 h showed **11c** (35%), $I_3AuPMe_3$ (35%), **7t** (27%), and **7c** (3%).

**$CF_3AuPMe_3$ and $CF_3Br$ or $CH_3I$.** In an NMR tube reaction analogous to the preparation of **11** by method A, $CF_3AuPMe_3$ (22 mg, 0.065 mmol) was added to an NMR tube that had previously been sealed to a ground glass joint. $CH_2Cl_2$ (0.5 mL) was distilled into the tube on a vacuum line, and $CF_3Br$ (2.0 mmol) was frozen into the reaction from a calibrated volume. The tube was flame sealed under vacuum with the solution still frozen. The reaction was heated for 6 h at 50 °C; $^{19}F$ and $^1H$ NMR showed essentially no reaction. A similar experiment with $CH_3I$ in place of $CF_3Br$ also showed no reaction.

**$(CF_3)_2AuI(PEt_3)$ (12). Method A.** This compound was prepared in a sealed NMR tube reaction using the general approach outlined for **11**, method A. $CF_3AuPEt_3$ (18 mg, 0.047 mmol) was added to an NMR tube that had previously been sealed to a ground glass joint. $CH_2Cl_2$ (0.5 mL) was distilled into the tube on a vacuum line, and $CF_3I$ (0.15 mmol) was frozen into the reaction from a calibrated volume. The tube was flame-sealed under vacuum. Although this reaction was much slower than the preparation of **11**, the $^{19}F$ NMR spectrum showed peaks attributable to **12c** (>95%) and **12t** (<5%) after 5 days at room temperature. The assignment of isomers was based on the close similarity of splitting patterns and coupling constants to **11c** and **11t**.

**Method B.** **12** was also prepared by iodine addition as in **11**, method C. **8t** (60%), **8c** (10%), and **12c** (30%) were identified by their $^{19}F$ NMR spectra.

**$t_{1/2}$ Studies for $CF_3I$ Addition to 1 and 2.** The relative rates of disappearance for **1** and **2** upon oxidative addition of $CF_3I$ were studied in sealed NMR tube reactions with *α,α,α*-trifluorotoluene used as an internal standard. The procedure for **2** is given as an example; an identical number of moles of all reagents was used in the procedure for **1**. $CF_3AuPEt_3$ (19 mg, 0.050 mmol) and *α,α,α*-trifluorotoluene (25 mg, 0.17 mmol) were added to an NMR tube that previously had been sealed to a ground glass joint. This mixture was freeze–pump–thaw degassed three times on a vacuum line, and 1 mL of $CH_2Cl_2$ was frozen into the tube. Trifluoromethyl iodide (0.20 mmol) was frozen into the reaction from a calibrated volume, and the tube was flame sealed under vacuum. The reaction was allowed to warm to room temperature and was monitored periodically by $^{19}F$ NMR. After ~100 h at 23 °C, one-half of **2** remained and **12** was the only fluorine-containing product. We thus approximated $t_{1/2} = 100$ h for this reaction. A similar procedure for **1** yielded $t_{1/2} = 10$ min and $t_{1/2}\,(2)/t_{1/2}\,(1) = 600$.

**$CF_3AuPPh_3$ and $CF_3I$.** This reaction was carried out in a sealed NMR tube with a procedure similar to that used to prepare **12**. The reaction was heated at 50 °C for 24 h, but no evidence was seen in the $^{19}F$ NMR for oxidative addition products.

**$Br_2AuCl(PPh_3)$ and $Hg(CF_3)_2$.** A solution of $Br_2AuCl(PPh_3)$ (50 mg, 0.076 mmol) and $Hg(CF_3)_2$ (50 mg, 0.15 mmol) in 1 mL of $CH_2Cl_2$ was prepared in the glovebox and sealed in an NMR tube under an argon atmosphere as described above for the $Hg(CF_3)_2$ + ClAuL studies. No reaction was observed in the $^{19}F$ NMR after 18 h at 50 °C. Another reaction using diglyme as the solvent was heated for 4 h at 150 °C, but no (trifluoromethyl)gold compounds were observed in the $^{19}F$ NMR.

**Reduction of Gold(III) Complexes by $Cd(CF_3)_2$·DME.** The reactions of a variety of gold(III) complexes with $Cd(CF_3)_2$·DME were examined in sealed NMR tubes. A representative example is given here. In the glovebox, $Cd(CF_3)_2$·DME (10 mg, 0.029 mmol) and $CF_3AuI_2(PMe_3)$ (30 mg, 0.051 mmol) were added to an NMR tube which previously had been sealed to a ground glass joint. A Teflon needle valve adapter was attached to the tube at the glass joint, and the assembly was removed from the glovebox. $CH_2Cl_2$ (1 mL) was frozen into the reaction mixture on a vacuum line, and the tube was flame sealed at −80 °C under an argon atmosphere. The reaction was warmed slowly to room temperature and monitored by $^{19}F$ NMR. After 6 h at room temperature, **7** was consumed and the only fluorine-containing species present were $CF_3AuPMe_3$, $CF_3I$, and $Cd(CF_3)_2$·DME. Similar reactions were carried out with the following gold(III) compounds: $CF_3AuBr_2(PMe_3)$, $CF_3AuBr_2(PEt_3)$, $CF_3AuBr_2(PPh_3)$, $Cl_3AuPEt_3$, $I_3AuPPh_3$, $ClAuI_2(PMe_3)$, and $ClAuBr_2(PPh_3)$. In all cases reduction to $CF_3AuL$ (with accompanying liberation of trifluoromethyl halide) was the predominant process.

**$(CF_3)_3AuPMe_3$ (13).** In the glovebox, $(CF_3)_2AuI(PMe_3)$ (0.45 g, 0.84 mmol) and $Cd(CF_3)_2 \cdot DME$ (0.58 g, 1.70 mmol) were added to the 25-mL heavy-walled reaction vessel described in the preparation of 11, method A. It was necessary to remove the Teflon needle valve to allow addition of the solids. The needle valve was replaced, and the reaction vessel was removed from the glovebox. $CH_2Cl_2$ (15 mL) was frozen into the vessel on a vacuum line, and $CF_3I$ (5.5 mmol) was measured into a calibrated volume and transferred to the reactor with liquid nitrogen cooling. The Teflon needle valve was closed, and the reaction mixture was heated at 60 °C for 12 h; the color of the solution remained pale yellow throughout the thermolysis. The reaction mixture was withdrawn via syringe and filtered. The solvent was removed from the filtrate in vacuo, and the solid residue was extracted with several portions of diethyl ether. This ether solution was taken to dryness, and the residue (0.36 g) was transferred to a sublimator where sublimation (75 °C, $10^{-4}$ Torr) onto a water-cooled probe gave 0.32 g (0.67 mmol) of white crystalline 13, 80% yield based on $(CF_3)_2AuI(PMe_3)$. MS: *m/e* (relative intensity) 461 (1.4), $(CF_3)_2(CF_2)AuPMe_3$; 411 (13), $(CF_3)_2AuPMe_3$; 323 (5.4), $CF_2AuPMe_3$; 273 (100), $AuPMe_3$. Anal. Calcd for $C_6H_9F_9PAu$: C, 15.01; H, 1.89; F, 35.62; P, 6.45. Found: C, 15.08; H, 1.83; F, 35.33; P, 6.36.

**$(CF_3)_2AuI(PMe_3)$ and $Cd(CF_3)_2 \cdot DME$.** In an NMR tube reaction, $(CF_3)_2AuI(PMe_3)$ (12 mg, 0.022 mmol), $Cd(CF_3)_2 \cdot DME$ (11 mg, 0.032 mmol), and 0.5 mL of $CH_2Cl_2$ were sealed under an argon atmosphere. The sample was heated overnight at 35 °C; the predominant products observed in the $^{19}F$ NMR spectrum were 1, 13, and $CF_3I$.

**$(CF_3)_2AuI(PMe_3)$ and $CF_3AuPMe_3$.** $CF_3AuPMe_3$ (25 mg, 0.046 mmol) and $(CF_3)_2AuI(PMe_3)$ (20 mg, 0.058 mmol) were added to an NMR tube sealed to a ground glass joint. On the vacuum line, 0.5 mL of $CH_2Cl_2$ was distilled into the mixture and the tube was flame sealed under argon. The sample was heated for 12 h at 40 °C and examined by $^{19}F$ NMR: The major resonances were due to the 1 and 11 starting materials; no evidence was seen for 13.

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**Registry No.** 1, 59963-16-5; **2**, 119970-84-2; **3**, 60898-04-6; **4t**, 119970-85-3; **4c**, 120052-42-8; **5t**, 119970-86-4; **5c**, 120052-43-9; **6t**, 119970-87-5; **7t**, 119970-88-6; **7c**, 120052-44-0; **8t**, 119970-89-7; **8c**, 120052-45-1; **9c**, 119970-90-0; **9t**, 120052-46-2; **10c**, 119970-91-1; **10t**, 120052-47-3; **11c**, 119970-92-2; **11t**, 120052-48-4; **12c**, 119970-93-3; **12t**, 120052-49-5; **13**, 107546-93-0; $CF_3I$, 2314-97-8; $CH_3I$, 74-88-4; $ClAuPMe_3$, 15278-97-4; $ClAuPEt_3$, 15529-90-5; $ClAuPPh_3$, 14243-64-2; $Cd(CF_3)_2 \cdot DME$, 76256-47-8; $Hg(CF_3)_2$, 371-76-6; $MeAuPMe_3$, 32407-79-7; $Br_3AuPMe_3$, 59110-29-1; $IAuPMe_3$, 25892-35-7; $I_3AuPMe_3$, 119970-94-4; $CF_3Br$, 75-63-8; $Cl_3AuPEt_3$, 56213-22-0; $O_3AuPPh_3$, 83971-98-6; $ClAuI_2(PMe_3)$, 119970-95-5; $ClAuBr_2(PPh_3)$, 32425-13-1.

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# (1*R*)-(−)-Nopol as the Source of an Optically Pure Fused Cyclopentadienyl Ligand. Stereochemical Course of Complexation to Cyclopentadienyltitanium and -zirconium Dichloride Fragments[1]

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The optically active pinane-related cyclopentadienide anion 4 has been complexed with $TiCl_3 \cdot 3THF$, $CpTiCl_3$, $ZrCl_4$, $CpZrCl_3$, and $Cp^*ZrCl_3$ for the purpose of assessing the level of $\pi$-facial stereoselectivity capable of being attained by this rather unusual ligand. In the homocomplexation experiments, the less hindered surface of 4 is utilized almost exclusively. At room temperature and above, the less sterically demanding Cp and Cp* ligands also exhibit a preference for coordination from above plane, although respectable levels of below-plane complexation now make their appearance. The dominance of above-plane reactivity ceases to persist when 4 is reacted with $CpTiCl_3$ and $CpZrCl_3$ at −78 °C. Under these circumstances, the proportion of 6 increases to 83% and 10 becomes the exclusive product. X-ray crystallographic data are provided for zirconocene 10.

Interest in optically active titanocene and zirconocene dichlorides has increased significantly in recent years in concert with a growing awareness of their ability to achieve stereodifferentiation in selected organic transformations.[3–5] Our thrust in this area has been to fuse a cyclopentadienyl

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[1] Paper 45 in the series dealing with isodicyclopentadienes and related molecules. For 44, see: Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D., submitted for publication.

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