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Formation of group 11 trifluoromethyl derivatives by reaction of $Cd(CF_3)_2 \cdot$ glyme with representative Au, Ag, and Cu complexes: isolation of $Au(CF_3)_3(PMe_3)$, $Au(CF_3)_3(PEt_3)$, $AuI(CF_3)_2(PMe_3)$, $AuCF_3(PMe_3)$, $AuCF_3(PEt_3)$ and $AgCF_3(PMe_3)$; observation of $CuCF_3(PMe_3)$

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Abstract

The reaction of $Cd(CF_3)_2 \cdot$ glyme, glyme = $CH_3OCH_2CH_2OCH_3$, with $AuBr(PMe_3)$ forms $AuCF_3(PMe_3)$ in 51% yield; that with $AuCl(PEt_3)$ results in $AuCF_3(PEt_3)$ in 67% yield. Trifluoromethyl iodide immediately oxidizes $AuCF_3(PMe_3)$ to $AuI(CF_3)_2(PMe_3)$, 98% *cis*, 2% *trans*, by means of a radical pathway. The interaction of $AuI(CF_3)_2(PMe_3)$ with $AuCF_3(PMe_3)$ slowly generates $Au(CF_3)_3(PMe_3)$. The radical reaction between CF_3I and $AuCF_3(PEt_3)$ eventually (12 d) forms $Au(CF_3)_3(PEt_3)$ and $AuI(PEt_3)$, but, at ambient temperature, the exposure of $AuCF_3(PEt_3)$ to C_2F_5I yields the pentafluoroethyl gold(I) complex, $AuC_2F_5(PEt_3)$, along with CF_3I and $AuI(CF_3)_2(PEt_3)$. No reaction between $AuBr(PEt_3)$ and CF_3I was observed. If PMe_3 is added to solutions that initially contained AgOAc and $Cd(CF_3)_2 \cdot$ glyme, $AgCF_3(PMe_3)$, 36%, is formed. Although observed by ^{19}F NMR, $CuCF_3(PMe_3)$ could not be isolated. In all cases examined the group 11 PMe_3 adducts were substantially more stable than the PEt_3 adducts. In the absence of light, the stabilities of the group 11 CF_3 complexes fall in the order $AuCF_3 > AgCF_3 > CuCF_3$.

Introduction

For some time we have been interested in trifluoromethyl organometallic compounds which we commonly synthesize by ligand exchanges between metal halides and $Cd(CF_3)_2 \cdot$ glyme, where glyme is $CH_3OCH_2CH_2OCH_3$ [1]. Our interest in the group 11 CF_3 derivatives was kindled by the observation that frequently the efficiency of these substitutions is dramatically enhanced by the addition of silver salts into the reaction medium [2]. However, although group 11 trifluoromethyl

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intermediates, e.g., $CuCF_3$, have been presumed in a variety of reactions [3*], relatively few studies have examined these types of compounds directly.

The first isolated group 11 CF_3 complexes were formed during Puddephatt's study of CF_3I reactions with $AuCH_3(PR_3)$, R = CH_3, Ph [4]. Later Lagow et al. synthesized $Au(CF_3)_3(PMe_3)$ and $[Au(CH_2)_2PPh_2]_2(CF_3)_2$ [5,6]. The formation of $AgCF_3$ from Ag atoms and CF_3I was indicated by hydrolysis [7], but the initial $AgCF_3$ spectroscopic data came from the reactions of Ag atoms with CF_3 radicals which, after the addition of PMe_3, yielded $AgCF_3(PMe_3)$ [5]. Additionally, Naumann [8] has reported the formation of $Ag(CF_3)_2^-$, $AgCF_3 \cdot$ glyme, and $Ag(CF_3)_4^-$ from $Cd(CF_3)_2 \cdot$ glyme and $AgNO_3$. Finally, Burton has generated three, as yet unidentified, $CuCF_3$ products from the interactions of $Cd/CuCl/CF_2Cl_2$ mixtures in DMF [9].

Fluorine-19 NMR spectra clearly indicated the presence of $AgCF_3$ species during our silver assisted trifluoromethylations of metal halides [2], but the literature data did not always allow reliable spectroscopic identification of which of the several $AgCF_3$ species might have been present. For example, the reported chemical shifts and Ag–F coupling constants for $AgCF_3(PMe_3)$ and $Ag[Ag(CF_3)_4]$ are exceptionally similar [5,8]; somewhat surprisingly neither Ag–P nor P–F coupling was observed in the former. In the present communication we report the results of a preliminary examination of the reactions of representative group 11 complexes with $Cd(CF_3)_2 \cdot$ glyme, carried out to determine how readily trifluoromethyl group 11 derivatives of, e.g., gold(III), could be generated by solution state reactions and to allow an initial comparison of the properties of analogous gold, silver, and copper CF_3 complexes.

Experimental

General

Unless otherwise indicated all of the manipulations described below were carried out in a standard vacuum line or under N_2 in a glove bag. The ^{19}F and ^{31}P $\{^1H\}$ NMR spectra, which are referenced to external CF_3CO_2H or 85% H_3PO_4, respectively, were recorded upon an IBM 200SY spectrometer; positive chemical shifts are deshielded from the reference. The mass spectral data were obtained from an HP 5985A instrument; the 15 eV source was maintained at 200 °C. The IR spectra are from an IBM 32/FTIR spectrophotometer. The uncorrected melting points were determined with a Thomas Hoover capillary melting point apparatus.

Dioxane and DMF were dried over KOH; CH_2Cl_2 and $CDCl_3$ over P_4O_{10}. Glyme, $CH_3OCH_2CH_2OCH_3$, and Et_2O were dried over sodium benzophenone ketyl. All were degassed immediately prior to use. Copper bromide (Aldrich) was dried under vacuum at 100 °C. Galvinoxyl (Aldrich), $AuCl(PEt_3)$ (Strem), AgOAc (Alfa), CF_3I (SCM) and C_2F_5I (PCR) were all used as received. Trimethylphosphine was derived from $[AgI(PMe_3)]_4$ (Aldrich) by thermolysis; PEt_3 was obtained from laboratory stock.

Bis(trifluoromethyl)cadmium · glyme was formed from $Hg(CF_3)_2$ and $CdMe_2$ in glyme [10]. The gold bromide complexes, e.g., $AuBr(PMe_3)$, were generated from

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* Reference numbers with asterisks indicate notes in the list of references.

$HAuCl_4 \cdot 3H_2O$ by standard methods [11], $AgNO_3(PPh_3)$ was prepared from $AgNO_3$ and PPh_3 (Aldrich) [12]. Their identities were confirmed by mass spectrometry.

Formation of (trifluoromethyl)gold(I) complexes

Preparation of $AuCF_3(PEt_3)$. Under N_2 $AuCl(PEt_3)$, 200 mg, 0.57 mmol, and $Cd(CF_3)_2 \cdot$ glyme, 200 mg (0.59 mmol), were added to a 10 ml reactor that was equipped with a Teflon valve and a Teflon coated magnetic stirrer. After the contents of the vessel had been manually mixed, the reactor was evacuated and CH_2Cl_2, 4 ml, was distilled onto the mixture after which the reactor was sealed. Upon warming, the solution became dark brown. Aside from the resonances associated with $Cd(CF_3)_2 \cdot$ glyme, the ^{19}F NMR spectra that were obtained from aliquots of the solution during the course of the reaction contained a large doublet at 47.5 ppm and much smaller (ca. 5–10%) singlets at 50.8 and 48.1 ppm. The first two were apparent within minutes, but that at 48 ppm was evident only after several hours. After stirring for 40 h, the pale pink solid that had been generated was separated from the lemon colored supernatant by filtration through a sintered glass funnel. The solvent was removed from the filtrate under reduced pressure and the product $AuCF_3(PEt_3)$, 146 mg (0.381 mmol), was isolated in 67% yield by sublimation at 100 ° C.

Once formed, trifluoromethyl(triethylphosphine)gold(I), a white crystalline material which melts at 66 ° C, is reasonably stable in air, but it does begin to decompose over the course of two days. The ^{19}F NMR spectrum of the compound in $CDCl_3$ consists of a doublet, $^3J(P–F)$ 44 Hz, at 47.6 ppm, see Table 1. The ^{31}P $\{^1H\}$ spectrum contains a quartet, $^3J(P–F)$ 44 Hz, at 35.7 ppm, see Table 1. Mass spectrum (m/e, ion, assignment): 365, $AuPEt_3CF_2$, 14%; 315, $AuPEt_3$, 55%, 168 PEt_3CF_2, 30%; 140, PEt_2HCF_2 100%, 118 PEt_3, 62%; 112, $PEtH_2CF_2$, 11%; 103, PEt_2CH_2, 10%; 90, PEt_2H, 95%; 69, CF_3, 8%. Ir absorptions (KBr) are found at 2966 (s), 2936 (m), 2876 (m), 1458 (m), 1417 (w), 1381 (w), 1123 (vs), 1093 (m), 1047 (vs), 974 (vs), 769 (s), and 756 (m) cm^{-1}. Anal: $C_7H_{15}AuF_3P$ calc.: C, 21.91; H, 3.94%; Found (Schwarzkopf) C, 21.79; H, 3.69.

Preparation of $AuCF_3(PMe_3)$. Methylene chloride, 4 ml, $AuBr(PMe_3)$, 150 mg (0.43 mmol), and $Cd(CF_3)_2 \cdot$ glyme, 150 mg (0.44 mmol), were taken as above and the resulting slurry was stirred for 24 h at ambient temperature after which time the purple solids were separated from the colorless supernatant by filtration. Removal of the material that was volatile at ambient temperature followed by sublimation of the remaining solids at 85–90 ° C yielded $AuCF_3(PMe_3)$, 74 mg (0.22 mmol), 51%. Fluorine NMR spectra (CH_2Cl_2) obtained from the unsublimed residue contained small resonances at 48.1 (s) and 50.8 (s) ppm.

Trifluoromethyl(trimethylphosphine)gold(I), a white solid which melts with decomposition at 191–193 ° C is stable in air for weeks. The ^{19}F and ^{31}P NMR spectral data (CH_2Cl_2) are collected in Table 1. Mass spectrum: 342, $AuPMe_3CF_3$, 2%; 323, $AuPMe_3CF_2$, 2%; 273, $AuPMe_3$, 100%; 258, $AuPMe_2$, 7%; 76 PMe_3, 5%; 61, PMe_2, 5%. No other ions were observed. IR absorptions (KBr) are found at 2914 (m), 1973 (w), 1425 (vs), 1312 (m), 1294 (vs), 1124 (vs), 1086 (m), 968 (vs), 854 (m), 752 (s), 694 (m), and 681 (m) cm^{-1}.

Formation of (trifluoromethyl)gold(III) complexes

Preliminary experiments. Reactions of $Cd(CF_3)_2 \cdot$ glyme with gold(III) halides. Bis(trifluoromethyl)cadmium · glyme was exposed to several gold(III) halides, in-

Table 1

^{19}F NMR data for monovalent group 11 trifluoromethyl complexes

(s = singlet; d = doublet; q = quartet)

Compound	$\delta(^{19}F)$ (ppm) [a]	$^{3}J(P-F)$ (Hz)	$^{2}J(Ag-F)$ (Hz) [b]
Au^{I} complexes			
$AuCF_3(PMe_3)$	47.9 (d)	48 [c]	
$AuCF_3(PEt_3)$	47.6 (d)	44 [d]	
$AuC_2F_5(PEt_3)$	−6.6 (s) (3F)	–	
	−29.7(d) (2F)	25	
Ag^{I} complexes			
$AgCF_3(PPh_3)$	53.2 (d)	– [e]	92
$Ag(CF_3)_2^-$	51.9 (d) [f]	– [e]	99
$[AgCF_3 \cdot Et_2O]_n$	46.3 (d)	– [e]	38
$[AgCF_3(PPh_3)]_n$	46.6 (d)	– [e]	39
$[AgCF_3(PMe_3)]_n$	46.7 (d) [g]	– [e]	40/39
Cu^{I} complexes			
$CuCF_3 \cdot DMF$	47.4 (s) [h]		
$CuCF_3(PMe_3)$	47.3 (d)	21	
$CuC_2F_5 \cdot DMF$	−5.6 (s) (3F)		
	−34.2 (s) (2F)		

[a] Versus external trifluoroacetic acid. Positive values deshielded. [b] Natural abundance of ^{109}Ag 48.18%. of ^{107}Ag 51.82%, $I = 1/2$ for both isotopes. Typically the differences between the $^{109}Ag-F$ and $^{107}Ag-F$ coupling constants are not resolved. [c] Versus external 85% H_3PO_4, $\delta(^{31}P)$ 0.2 (q) ppm, $^{3}J(P-F)$ 48 Hz. Lit. [4] $\delta(^{19}F)$ 46.5 (d) ppm, $J(P-F)$ 48.3 Hz. [d] Versus external 85% H_3PO_4, $\delta(^{31}P)$ 35.7 (q) ppm., $^{3}J(P-F)$ 44 Hz. [e] P–F coupling not observed at ambient temperature. [f] Lit. [8] $\delta(^{19}F)$ 53.5 (dd) ppm (py); $J(Ag-F)$ 100/87 Hz. [g] Versus external 85% H_3PO_4, $\delta(^{31}P)$ −36.3 (s) ppm. Lit [5] $\delta(^{19}F)$ 46.5 (d) Hz, $J(Ag-F)$ 40.7 Hz; $\delta(^{31}P)$ (−) 37.6 ppm. [h] Lit. [9]. $\delta(^{19}F)$ (Species *B*) 45.7 ppm.

cluding $AuBr_3(PEt_3)$, in a variety of solvents. Although sequential trifluoromethylation of $AuBr_3(PEt_3)$ to ultimately form $Au(CF_3)_3(PEt_3)$ (see below) was observed at 0 °C in ether, for example, the major products observed in all of these reactions were CF_3Br and the monovalent gold complex $AuCF_3(PEt_3)$. The ^{19}F NMR data [13*] indicated that while substantial amounts of $AuBr(CF_3)_2(PEt_3)$ were generated, the amount of $Au(CF_3)_3(PEt_3)$ that was present never exceeded ca. 10%. Similarly, ^{19}F spectra obtained from the reactions between *cis*-$AuI(CF_3)_2(PMe_3)$ (see below) and $Cd(CF_3)_2 \cdot$ glyme contained large resonances from $AuCF_3(PMe_3)$ and CF_3I, but in the absence of added CF_3I [14*] only traces, ca. 5%, of $Au(CF_3)_3(PMe_3)$ were observed.

Interaction of excess CF_3I with $AuBr(PEt_3)$. (Triethylphosphine)gold bromide, 200 mg (0.51 mmol), CF_3I, 111 mg (0.566 mmol), and CH_2Cl_2, 1 ml, were sealed into a 4 mm tube that was maintained at ambient temperature for 30 d. No evidence for reaction was obtained by ^{19}F NMR.

Preparation of $AuI(CF_3)_2(PMe_3)$. Freshly sublimed $AuCF_3(PMe_3)$, 25 mg (0.073 mmol), was placed into a 4 mm Pyrex tube which was then connected to the vacuum line, cooled to −196 °C, and evacuated. Trifluoromethyl iodide, 40 mg (0.204 mmol), and CH_2Cl_2, 2 ml, were vacuum distilled into the reactor which was sealed and brought to ambient temperature. Within 8 min, the solution became pale yellow. After 20 min, the resonances of $AuCF_3(PMe_3)$ were no longer evident in the

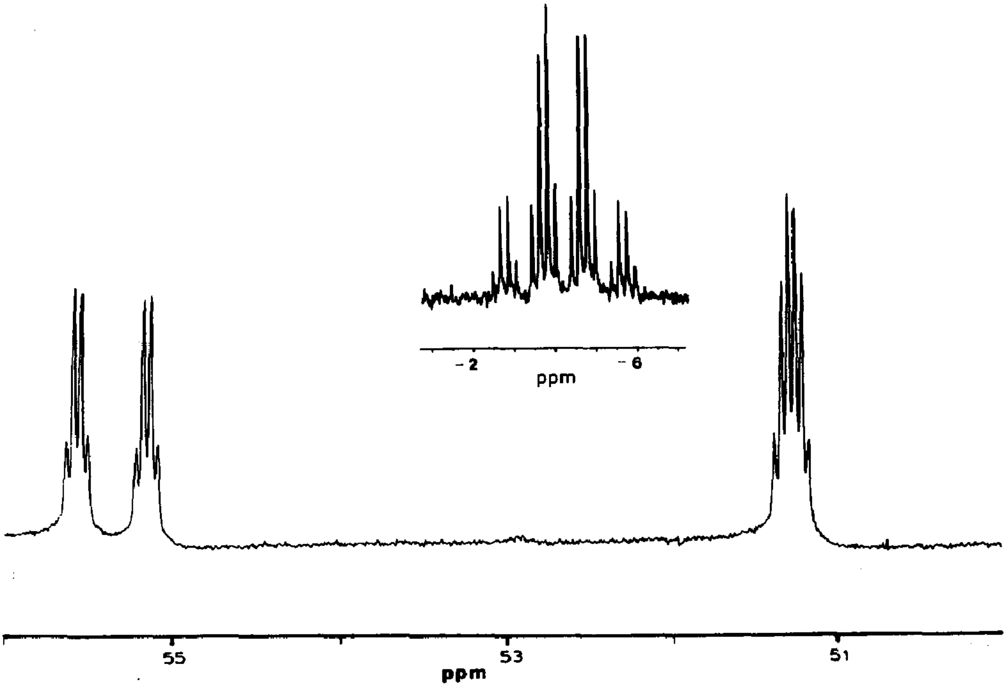

Fig. 1. The ^{19}F and ^{31}P (inset) spectra of *cis*-AuI$(CF_3)_2(PMe_3)$ obtained from the reaction of $AuCF_3(PMe_3)$ with excess CF_3I. The doublet of quartets to the left arises from the CF_3 group *trans* to PMe_3. The relative intensities of the ^{19}F resonances are 1.01/1.00.

^{19}F NMR spectrum and the only absorptions observed were those arising from the excess CF_3I and AuI$(CF_3)_2(PMe_3)$, see Fig. 1 and Table 2.

The reactor was then opened and the material that was volatile at ambient temperature removed, leaving a pale yellow powder, AuI$(CF_3)_2(PMe_3)$, which had formed quantitatively, 39 mg. Although both the *cis* and the *trans* isomers of the

Table 2

^{19}F and ^{31}P NMR data for trivalent group 11 trifluoromethyl complexes [a]

(d = doublet; q = quartet; h = heptet; m 1 = apparent 1/4/6/4/1 pentet, m 2 = apparent 1/3/4/4/3/1 sextet)

Compound	$\delta(^{19}F)$ [b]	$\delta(^{19}F)$ [c]	$\delta(^{31}P)$	$^3J(P-F)$ [b]	$^3J(P-F)$ [c]	$^4J(F-F)$
Au^{III} complexes						
trans-AuI$(CF_3)_2(PMe_3)$	58.3 (d)		11.7 (h)	11		
cis-AuBr$(CF_3)_2(PEt_3)$	54.3 (m 1)	48.5 (dq)		10	73	9
cis-AuI$(CF_3)_2(PEt_3)$	52.8 (m 1)	55.3 (dq)	27.8 (qq)	11	74	8
cis-AuI$(CF_3)_2(PMe_3)$	51.2 (m 2)	55.3 (dq)	−4.2 (qq)	16	78	8
$Au(CF_3)_3(PEt_3)$	48.0 (m 1)	44.8 (dh)	34.3 (qh)	7	74	6.7
$Au(CF_3)_3(PMe_3)$	47.0 (m 2)	45.3 (dh)		13	79	6.5
Ag^{III} complex						
$Ag(CF_3)_4^-$	46.2 (dd)					

[a] Chemical shifts in ppm vs. ext. TFA or 85% H_3PO_4; positive values deshielded. Coupling constants in Hz. [b] CF_3 group(s) *cis* to the phosphine ligand. [c] CF_3 group *trans* to the phosphine ligand. [d] Lit. [5] $\delta(^{19}F)$ 45.9 [b]; 44.1 [c], $^3J(P-F)$ 81.3 Hz.

compound are generated, see Table 2, the maximum amount of the *trans* isomer formed under the conditions utilized here is 2%. The melting point of $AuI(CF_3)_2(PMe_3)$, as obtained, is 139–141°C (dec). Mass spectrum: 538, $AuI(CF_3)_2(PMe_3)$, 6%; 469 $AuI(CF_3)PMe_3$, 24%; 411 $Au(CF_3)_2(PMe_3)$, 4%; 400, $AuI(PMe_3)$, 8%; 273, $AuPMe_3$, 100%; 203, PMe_3I, 26%; 76, PMe_3, 7%. No other ions were observed.

When the above reaction was carried out in Et_2O or acetone rather than CH_2Cl_2, the oxidative-addition of CF_3I to $AuCF_3(PMe_3)$ was also completed very rapidly, ca. 15 min, but there was a slightly larger amount of the *trans* isomer formed, ca. 4%.

Generation of $AuI(CF_3)_2(PMe_3)$ *in the presence of galvinoxyl.* Freshly sublimed $AuCF_3(PMe_3)$, 20.0 mg (0.058 mmol), and galvinoxyl, 1.00 mg (0.0023 mmol), were placed into a 4 mm tube which was then evacuated. Methylene chloride, 1 ml, and CF_3I, 50 mg (0.26 mmol), were distilled onto the solids. The vessel was sealed and the interaction was followed by ^{19}F NMR.

During the first five days, no reaction was observed, but thereafter the brown color of the galvinoxyl slowly lessened. Simultaneously, the resonances of $AuI(CF_3)_2(PMe_3)$ began to grow into the spectra. After 14 d, the only resonances in the ^{19}F spectra from (trifluoromethyl)gold compounds were those of $AuI(CF_3)_2$-(PMe_3), 98% *cis*, 2% *trans*.

Preparation of $Au(CF_3)_3(PMe_3)$. Trifluoromethyl(trimethylphosphine)gold(I), 10 mg, 0.029 mmol), and $AuI(CF_3)_2(PMe_3)$, 10 mg (0.019 mmol), were introduced into a 4 mm reactor which was evacuated and CH_2Cl_2, 1 ml, was added. The vessel was sealed, maintained at ambient temperature, and the progress of the reaction was monitored by ^{19}F NMR. After 4 h, a very small new resonance was found at 47 ppm. After 2 days, in addition to those of CF_3H, two resonances, the one at 47 ppm and a second centered at 45.3 were present in intensities comparable to the residual *cis*-$AuI(CF_3)_2(PMe_3)$. After 12 d ^{19}F NMR indicated that $AuCF_3(PMe_3)$ and $Au(CF_3)_3(PMe_3)$ were present in the molar ratio 0.8/1.0 and $AuI(CF_3)_2(PMe_3)$ was no longer observed. After the reaction was terminated mass spectrometry and ^{31}P NMR both indicated that the amounts of $Au(CF_3)_3PMe_3$ and $AuI(PMe_3)$ that had formed were equivalent. The identity of the gold(III) product was confirmed by ^{19}F NMR (see Table 2) and mass spectrometry ($M-F$, $M-CF_3$ ions) [5] after the residual $Au(CF_3)_3(PMe_3)$, 23%, had been separated by sublimation (80°C).

Generation of $AuI(CF_3)_2(PEt_3)$ *and* $Au(CF_3)_3(PEt_3)$. One ml of CH_2Cl_2 and 0.203 mmol CF_3I were sequentially condensed onto 22.0 mg (0.057 mmol) of $AuCF_3(PEt_3)$, then the vessel was sealed and the ambient temperature reaction was followed by ^{19}F NMR. After 30 min, during which time the originally clear, colorless solution had become pale yellow, the resonances of *cis*-$AuI(CF_3)_2(PEt_3)$ were clearly evident. The only other resonances in the spectrum were those arising from CF_3I and $AuCF_3(PEt_3)$, see Fig. 2. The relative molar ratio of $AuCF_3(PEt_3)$, $AuI(CF_3)_2(PEt_3)$ at this time was 1.00/0.94. After 3.5 h, Fig. 3, the intensities of the $AuCF_3(PEt_3)$ resonances in the ^{19}F NMR had decreased substantially and the ^{31}P spectrum contained the resonances of the gold complexes in the relative ratio 1/5, see inset. The resonances of a third (trifluoromethyl)gold complex, $Au(CF_3)_3(PEt_3)$, were first observed after 12 h. After 210 h the resonances of $Au(CF_3)_3(PEt_3)$ dominated the ^{19}F spectrum, see Fig. 4. At this time the ^{31}P NMR spectrum contained the resonances of both $AuI(PEt_3)$ 40 ppm, and $AuI_3(PEt_3)$ 46 ppm, (10/1 intensity ratio) in addition to those of $Au(CF_3)_3(PEt_3)$.

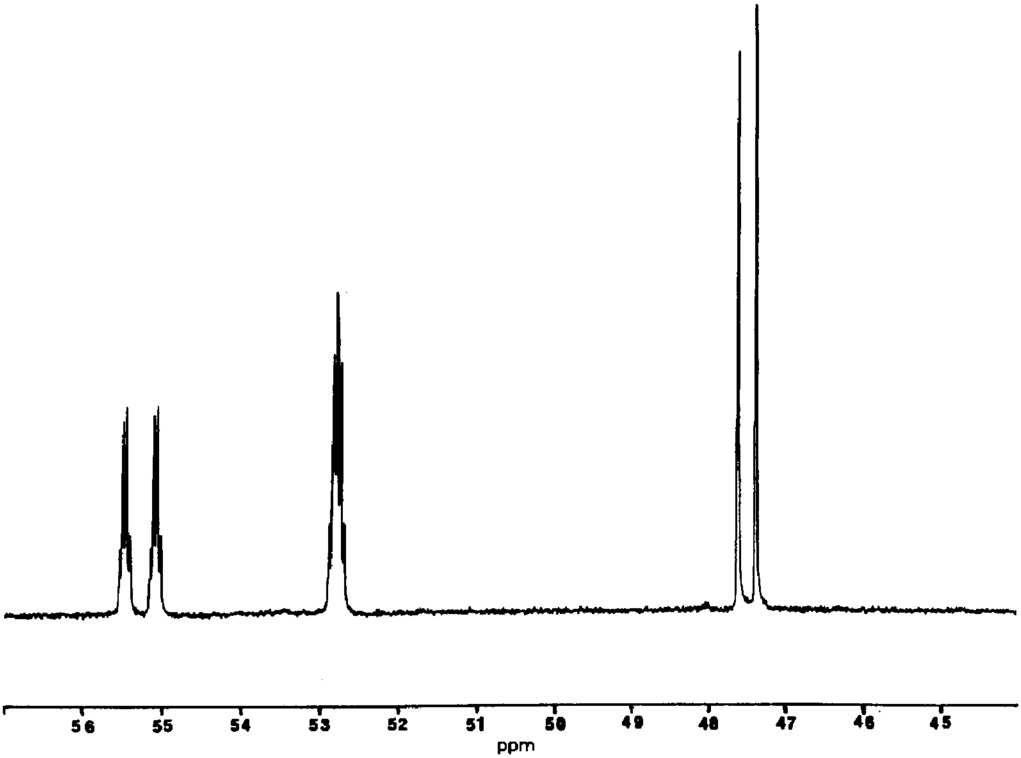

Fig. 2. The ^{19}F NMR spectrum from the reaction of $AuCF_3(PEt_3)$ with excess CF_3I after 30 min. The doublet of quartets and apparent quintet arise from *cis*-$AuI(CF_3)_2(PEt_3)$, the doublet from $AuCF_3(PEt_3)$. The relative molar ratios indicated by ^{19}F NMR are 1.00/1.06, respectively. Not shown: CF_3I, 72 ppm.

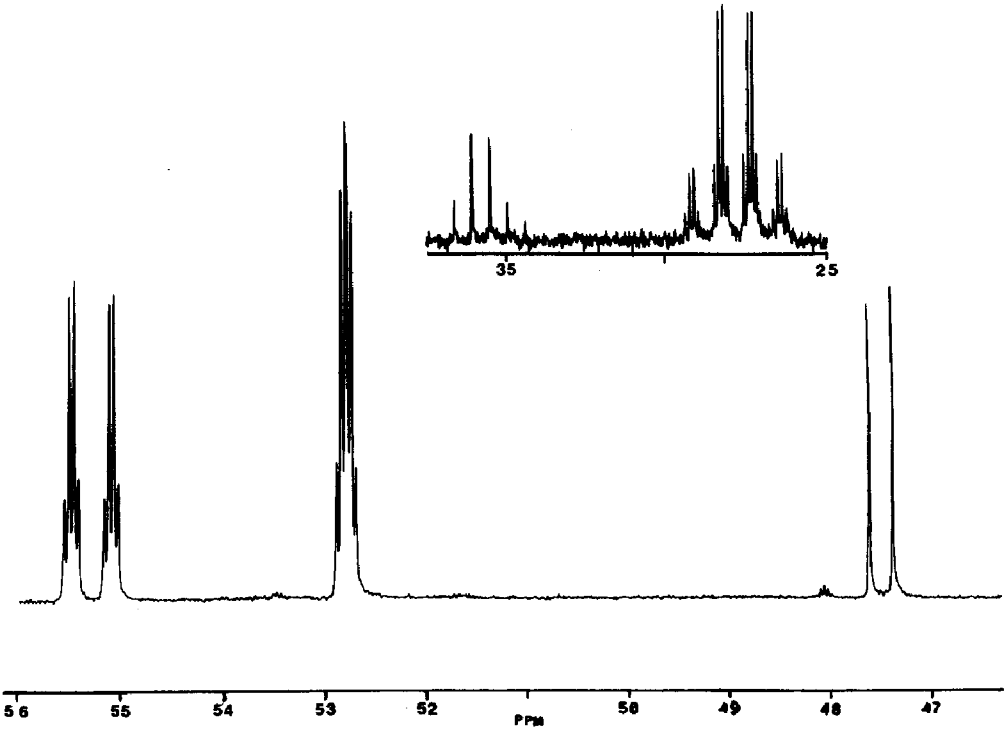

Fig. 3. The ^{19}F and ^{31}P (inset) NMR spectra from the reacton of $AuCF_3(PEt_3)$ with excess CF_3I after 3.5 h. Not shown: CF_3I, 72 ppm.

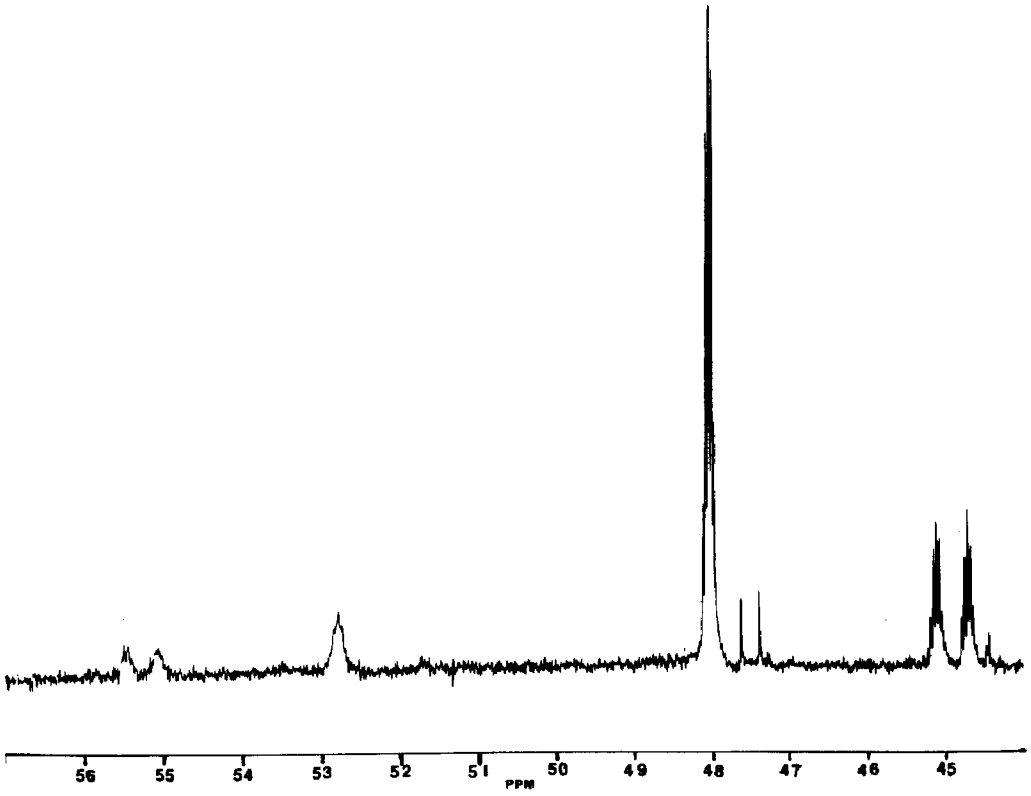

Fig. 4. The ^{19}F NMR spectrum of the reaction of $AuCF_3(PEt_3)$ with excess CF_3I after 210 h. The resonances on the left are from *cis*-$AuI(CF_3)_2(PEt_3)$, those at 48 and 44.8 ppm from $Au(CF_3)_3(PEt_3)$, and those at 47.6 ppm from $AuCF_3(PEt_3)$. The ^{19}F spectrum indicates that these compounds are present in the relative molar amounts 1.48/4.90/1.00. Not shown: CF_3I, 72 ppm.

After 290 h, the brown solids formed were separated by filtration and, after removal of the volatile material, $Au(CF_3)_3(PEt_3)$ was sublimed from the filtrate at 85 ° C, see Fig. 5. The yields from different preparations of the type described above varied, but were typically ca. 20–50%, see discussion.

Generation of $AuI(CF_3)_2(PEt_3)$ and $Au(CF_3)_3(PEt_3)$ in the presence of galvinoxyl. Trifluoromethyl iodide, 0.100 mmol, and CH_2Cl_2, 1 ml, were condensed into a 4 mm reactor containing $AuCF_3(PEt_3)$, 0.026 mmol, and galvinoxyl, 0.0012 mmol. The vessel was sealed and warmed to ambient temperature, resulting in a brown solution. Fluorine NMR spectra taken during the first 20 d of the reaction contained only the resonances derived from the reagents. After 33 days, however, the solution had become a pale yellow, and the spectra indicated that both $AuI(CF_3)_2PEt_3$ and $Au(CF_3)_3PEt_3$ had formed. The molar ratios $AuCF_3(PEt_3)$/*cis*-$AuI(CF_3)_2(PEt_3)$/$Au(CF_3)_3(PEt_3)$ indicated by ^{19}F NMR were 1.0/1.1/0.1. After 55 d the relative ratios were 1.0/7.1/2.3, respectively.

Exposure of $AuCF_3(PEt_3)$ to C_2F_5I. In a sealed tube CH_2Cl_2, 1 ml, and C_2F_5I, 2 mmol, were allowed to interact with $AuCF_3(PEt_3)$, 0.1 mmol. After 20 min at ambient temperature, in addition to those of the reagents, the absorptions due to CF_3I (72 ppm) and *cis*-$AuI(CF_3)_2(PEt_3)$ were evident in the ^{19}F spectrum along with a singlet at −6.6 ppm and a doublet, J(P–F) 25 Hz, at −29.7 ppm the last

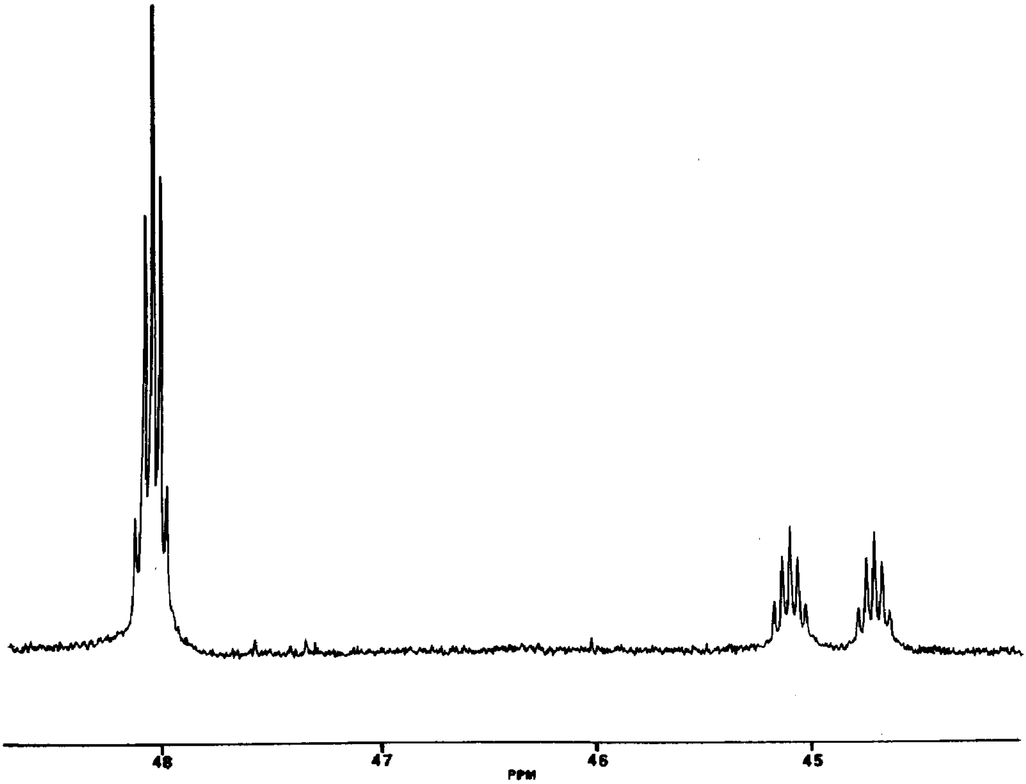

Fig. 5. The ^{19}F NMR spectrum of $Au(CF_3)_3(PEt_3)$. The doublet of heptets on the right arises from the CF_3 group *trans* to PEt_3. The relative intensities of the resonances are 1.98/1.00.

two in a 3/2 intensity ratio. After 60 min the mole ratio $AuCF_3(PEt_3)$ to $AuC_2F_5(PEt_3)$ was 1.0/1.7. During the 24 h duration of the experiment no resonances that could have been ascribed to a pentafluoroethylgold(III) complex were observed.

Formation of (trifluoromethyl)silver complexes

Exposure of AgOAc to $Cd(CF_3)_2 \cdot$ glyme in Et_2O. When AgOAc, 50.0 mg (0.299 mmol), and $Cd(CF_3)_2 \cdot$ glyme, 75 mg (0.221 mmol), were sealed into a 4 mm Pyrex reactor with Et_2O, 1 ml, a vigorous reaction occurred yielding a black solid and a colorless supernatant. The initial ^{19}F NMR spectrum (10 min) contained the resonances of three products: CH_3COF, 127 (q) ppm, *J*(H–F) 7 Hz, CF_3H, −1.0 (d) ppm, *J*(H–F) 80 Hz, and an $AgCF_3$ species, 46.3 (d) ppm, *J*(Ag–F) 38 Hz, see discussion; $Cd(CF_3)_2 \cdot$ glyme was not observed. Over the next 12 days, during which time the reactor was covered with Al foil except when in the spectrometer, CF_3H was evolved and the resonances from the $AgCF_3$ species decreased in intensity with a half-life of ca. 2 days.

Exposure of $AgNO_3(PPh_3)$ to $Cd(CF_3)_2 \cdot$ glyme in glyme and CH_2Cl_2. Glyme, 1 ml, $Cd(CF_3)_2 \cdot$ glyme, 50 mg, and $AgNO_3(PPh_3)$, 75 mg, were sealed into a 4 mm Pyrex reactor. The ^{19}F spectrum taken 10 min after warmup contained the resonances of two $AgCF_3$ complexes, at 51.9 (d) ppm, *J*(Ag–F) 99 Hz, and at 53.2 (d) ppm, *J*(Ag–F) 92 Hz, in a 5/1 intensity ratio, along with the residual $CdCF_3$

resonances and those of a small amount of CF_3H, see Table 1. Twenty h later the spectrum was unchanged.

When a similar reaction was carried out in CH_2Cl_2, there were again two $AgCF_3$ resonances in a 5/1 intensity ratio, but now the chemical shifts were at 51.4 (d) ppm, J(Ag–F) 100 Hz and at 46.6 (d) ppm, J(Ag–F) 39 Hz. The reactor contents were exposed to the atmosphere overnight and the resulting solid extracted with $CDCl_3$. The ^{19}F spectrum then indicated the presence of only one compound, 46.3 (dd) ppm, J(109/107 Ag–F) 40.3/35.7 Hz. This last product does not sublime, is sensitive to neither light nor air and is soluble in and stable toward water for periods of at least 30 days. No mass spectrum could be obtained.

Preparation of $AgCF_3(PMe_3)$. Silver acetate, 100.0 mg (0.598 mmol), and $Cd(CF_3)_2 \cdot$ glyme, 200.0 mg (0.599 mmol), were allowed to interact in Et_2O, 3 ml, for 10 min resulting in a dark brown solution. Trimethylphosphine, 44 mg (0.58 mmol), was then condensed into the 10 ml vessel and the resulting slurry stirred for 60 min at ambient temperature. With minimal exposure to light, the black solution was filtered through a sintered glass funnel and the volatile material removed from the filtrate, leaving 56 mg of a white powder, $AgCF_3(PMe_3)$, 36%.

At ambient temperature the ^{19}F NMR spectrum of $AgCF_3(PMe_3)$, in $CDCl_3$ is centered at 46.7 (d) PPM, J(Ag–F) 40/39 Hz and the ^{31}P NMR spectrum, a broad singlet is found at −36.3 ppm. Mass spectrum: 235/233, $AgCF_2(PMe_3)$, 14% each; 185/183 $Ag(PMe_3)$, 44% each; 95 PMe_3F, 19%; 76, PMe_3, 100%, 69 CF_3, 13%; 61 PMe_2, 63%. Further characterization was precluded by the extreme sensitivity of the compound to light and the atmosphere.

Formation of (trifluoromethyl) copper complexes

Reaction of CuBr with $Cd(CF_3)_2 \cdot$ glyme. Dried CuBr, 50.0 mg (0.347 mmol), and $Cd(CF_3)_2 \cdot$ glyme, 100.0 mg (0.247 mmol), were placed into a Pyrex reactor. After evacuation, 1 ml of DMF was added and the vessel was sealed, then allowed to warm to ambient temperature. During the first 10 min a vigorous reaction took place which resulted in the formation of a grey solution. After 10 min the ^{19}F NMR spectrum was dominated by two resonances, at 50.9 (s) and 47.4 (s) ppm, with the latter twice as intense. After 1 h, however, the intensity of the resonance at 47.4 ppm had decreased to ca. 50% of that at 50.9 ppm. During the next 10 h they both decreased proportionately, as CuC_2F_5, −5.6 (s) ppm (3F); −34.2 (s) ppm (2F) was formed. Other minor resonances at −1.2 (s) ppm and −104 (s) ppm were present, but no absorption near 43 ppm was observed.

When 1.04 mmol CuBr and 0.735 mmol $Cd(CF_3)_2 \cdot$ glyme were dissolved in 3 ml of DMF then, after 10 min, 1.00 mmol of PMe_3 was added, the course of the reaction was very similar, but 36 h were required for the analogous conversion of the initially formed material to CuC_2F_5. The resonances of only one new species were observed, 47.3 (d) ppm, J 21 Hz, but the compound could not be isolated.

Results and discussion

(Trifluoromethyl)gold(I) complexes

Although $Hg(CF_3)_2$ did not react with the gold(I) halides examined, the cadmium reagent, $Cd(CF_3)_2 \cdot$ glyme, readily generated $AuCF_3(PMe_3)$ and $AuCF_3(PEt_3)$ in 51 and 67% yields, respectively. Once formed, these derivatives were easily separated from the involatile by-products of the reaction by sublimation. The PMe_3 and PEt_3 adducts of $AuCF_3$ are quite similar in most respects but they do differ in that $AuCF_3(PMe_3)$ is significantly more stable toward the atmosphere than $AuCF_3(PEt_3)$ since the former survives exposure for several weeks seemingly unchanged whereas the latter begins to decompose within two or three days. The difference is presumably a reflection of the more effective coordinating ability of the PMe_3 ligand as is also evidenced by the differences in the ^{31}P chemical shift between the coordinated and the free ligands, $\Delta\delta(^{31}P)$, 62.2 ppm (PMe_3) vs. 55.8 ppm (PEt_3) [15*] and the magnitude of the PF coupling in the adducts, 48 Hz (PMe_3) vs. 44 Hz (PEt_3). The ^{19}F NMR data from $AuCF_3(PMe_3)$ obtained in this study are in accord with those previously reported by Puddephatt, who obtained very small amounts of the compound from the decomposition of $AuMe_2(CF_3)(PMe_3)$ [4]; $AuCF_3(PEt_3)$ was previously unreported.

(Trifluoromethyl)gold(III) complexes

In view of the ease with which the gold(I) trifluoromethyl complexes had been synthesized by reaction of the halides with $Cd(CF_3)_2 \cdot$ glyme, it was initially somewhat surprising that the seemingly analogous trifluoromethylation reactions of the gold(III) species, e.g., $AuBr_3(PEt_3)$ or $AuI(CF_3)_2(PMe_3)$, did not result in tris(trifluoromethyl)gold(III) derivatives in more than a few per-cent yield. The ^{19}F spectra did indicate that significant amounts of the dialkylated $AuBr(CF_3)_2(PEt_3)$ were formed in the first reaction, but in the absence of added CF_3I [14*], the phosphine containing products that were obtained from these reactions were predominantly those that arise from the reductive-elimination of the appropriate trifluoromethyl halide from the gold(III) center, rather than those derived from the trifluoromethylation of the last halide. Although the reduction of the gold(III) species was less rapid when the trifluoromethylation reactions were attempted at lower temperatures, in the absence of added CF_3I the amounts of $Au(CF_3)_3(PR_3)$, R = Me, Et, generated were never large enough to be synthetically useful.

When the gold(I) complex $AuCF_3(PMe_3)$ was exposed to an excess of trifluoromethyl iodide in CH_2Cl_2 the only reaction observed, see Fig. 1, was the immediate, quantitative oxidation of the gold substrate to $AuI(CF_3)_2(PMe_3)$ (eq. 1). The fact that the oxidative additions of CF_3I could be quenched for extended periods by the addition of small amounts of the radical scavenger galvinoxyl is taken as strong evidence that the additions of CF_3I to both $AuCF_3(PMe_3)$ and $AuCF_3(PEt_3)$ are radical in character and thus mechanistically analogous to the reaction of CF_3I with $AuCH_3(PMe_3)$ [4].

$$AuCF_3(PMe_3) + CF_3I \rightarrow \underset{\text{(ca. 100\%)}}{AuI(CF_3)_2(PMe_3)} \qquad (1)$$

Aside from *cis*-$AuI(CF_3)_2(PMe_3)$, the only other (trifluoromethyl)gold species generated in this reaction was a small amount of the *trans* isomer (2%). The two are readily distinguished by either ^{19}F or ^{31}P NMR, see Table 2.

When $AuCF_3(PEt_3)$ was similarly exposed to excess CF_3I, however, the overall reaction was different in character. Rather than immediate and complete oxidation to a gold(III) species as observed for $AuCF_3(PMe_3)$, the reaction between CF_3I and $AuCF_3(PEt_3)$ came to an apparent equilibrium as shown in eq. 2. Figures 2–4 clearly demonstrate the prolonged presence of both oxidation states of gold during this reaction.

$$\underset{\text{(ca. 15\%)}}{AuCF_3(PEt_3)} + CF_3I \leftrightarrows \underset{\text{(ca. 85\%)}}{AuI(CF_3)_2(PEt_3)} \quad (2)$$

The final gold containing product, $Au(CF_3)_3(PEt_3)$, first became evident in the spectra after 12 h and, although small amounts of $AuI_3(PEt_3)$, ca. 10%, were also observed, the ^{31}P NMR data are consistent with the interpretation that $Au(CF_3)_3(PEt_3)$ predominantly arises from ligand interchange between $AuCF_3(PEt_3)$ and $AuI(CF_3)_2(PEt_3)$ as shown in eq. 3 [16*].

$$AuCF_3(PEt_3) + AuI(CF_3)_2(PEt_3) \rightarrow AuI(PEt_3) + Au(CF_3)_3(PEt_3) \quad (3)$$

The apparent differences in the reactions of the two gold compounds with CF_3I are most easily interpreted in terms of the differences in the effective basicity of the two phosphine ligands which results in an enhanced thermal stability for the $Au^{III}(PMe_3)$ adducts relative to the PEt_3 adducts. In effect, this increased stability of the $Au^{III}(PMe_3)$ species suppresses the (presumed) back reaction in eq. 1 relative to that of eq. 2. Thus upon the addition of excess CF_3I to $AuCF_3(PMe_3)$, the latter compound is essentially completely removed from solution and is unavailable to serve as a CF_3 donor toward $AuI(CF_3)_2(PMe_3)$. As a test of the hypothesis, $AuCF_3(PMe_3)$ was added to $AuI(CF_3)_2(PMe_3)$ which had been separately prepared. The ligand exchange reaction between the gold(I) and the gold(III) centers analogous to that in eq. 3 then proceeded steadily, and at a rate compartable to that previously observed in the formation of $Au(CF_3)_3(PEt_3)$ from $AuCF_3(PEt_3)$ and CF_3I.

As was previously found for the trifluoromethylgold(I) compounds, the P–F coupling constants of the $Au^{III}PMe_3$ adducts are greater than those of the corresponding $Au^{III}PEt_3$ adducts, see Table 2. One of the more readily visible consequences of this difference is that (at 188 MHz) the resonances of the CF_3 groups *cis* to the PMe_3 ligands appear as sextets, whereas the resonances of the CF_3 groups *cis* to the PEt_3 ligands have the appearance of pentets, cf. Fig. 1 and 5.

Both the PMe_3 and PEt_3 ligands are prone to displacement by, e.g., (Lewis) basic solvents [17*], and the problem is more severe for the PEt_3 containing compounds. It was for this reason that sublimation was employed for the separations of the $Au(CF_3)_3$ trialkylphosphines from the slightly less volatile gold(I) and iodo gold(III) impurities, rather than, e.g., column chromatography or recrystallization, even though the yields obtained by this procedure, 20–50%, were substantially reduced from those indicated by the ^{19}F NMR spectrum of the intact samples. Once isolated, the properties of $Au(CF_3)_3(PMe_3)$ were in accord with those previously reported by Lagow [5], although F–F coupling was not observed in the original ^{19}F spectrum [5].

The differences between the reactions of CF_3I and C_2F_5I with $AuCF_3(PEt_3)$ are most easily attributed to the relative stabilities of the gold(III) products arising from the two compounds. Experimentally, the reaction of C_2F_5I with $AuCF_3(PEt_3)$ resulted in the formation of $AuC_2F_5(PEt_3)$ and CF_3I, part of which (ca. 50%) oxidatively-added to $AuCF_3(PEt_3)$ to form $AuI(CF_3)_2(PEt_3)$, as shown in eq. 2. No evidence for a pentafluoroethylgold(III) complex was obtained. Presumably, the mechanism for this transformation involves the oxidative-addition of C_2F_5I to

$AuCF_3(PEt_3)$, resulting in the relatively unstable (and unobserved) $AuI(C_2F_5)(CF_3)(PEt_3)$ which either eliminates C_2F_5I (regenerating the reagents) or CF_3I (resulting in the products shown in eq. 4). Collectively, these reactions strongly suggest that C_2F_5 is less able to stabilize the trivalent state of gold than CF_3.

$$AuCF_3(PEt_3) + C_2F_5I \rightleftharpoons [AuI(C_2F_5)(CF_3)(PEt_3)] \rightleftharpoons AuC_2F_5(PEt_3) + CF_3I \quad (4)$$

Similarly, the bis(trifluoromethyl)gold iodides are much more prone to decomposition than the analogous $Au(CF_3)_3(PR_3)$ complexes during workup, which suggests that, either thermodynamically or kinetically, the CF_3 group stabilizes gold(III) centers toward reductive elimination more efficiently than iodide does. Finally, the fact that no reaction was observed between $AuBr(PEt_3)$ and CF_3I may well be an indication that the trifluoromethyl ligand stabilizes gold(III) more effectively than bromide.

(Trifluoromethyl)silver(I) complexes

After 20 days at ambient temperature neither AgI nor $[AgI(PMe_3)]_4$ was found to react with $Cd(CF_3)_2 \cdot$ glyme, but silver substrates containing acetate or nitrate form $AgCF_3$ complexes within 5 min. Once generated, however, these species are much more difficult to isolate and examine than the analogous gold(I) compounds. Numerous attempts to isolate the readily generated $AgCF_3(PEt_3)$ were unsuccessful. Even the more stable $AgCF_3(PMe_3)$ was isolated in poor yield, 36%. Both $AgCF_3(PMe_3)$ and $AgCF_3(PEt_3)$ are very photosensitive.

The 11 ppm difference between the ^{19}F NMR chemical shifts that have been reported for $AgCF_3(PMe_3)$ [5], 46.5 ppm, and $AgCF_3 \cdot$ glyme, 57.7 ppm [8] initially seemed unusually large for compounds that differ only by the substitution of a "spectator" ligand. The most plausible interpretation of these results is that they reflect different states of aggregation of the $AgCF_3$ species in the different solvents.

In the most basic of the solvents employed here, glyme, the reaction of $AgNO_3(PPh_3)$ with $Cd(CF_3)_2 \cdot$ glyme resulted in the formation of two $AgCF_3$ species, $Ag(CF_3)_2^-$, 51.9 ppm [8], and (presumably) $AgCF_3(PPh_3)$, 53.2 ppm, in a 2.5/1 molar ratio; no resonances near 47 ppm were observed. When the reaction between the same two reagents was examined in the less polar CH_2Cl_2, however, there were again two $AgCF_3$ species formed, $Ag(CF_3)_2^-$ and $Ag(CF_3)(PPh_3)$, again in the same molar ratio, but here the chemical shift of the latter was 46.6 ppm, rather than 53.2 ppm; no resonances were observed in the 53 ppm chemical shift region. Similarly, in all of the silver trifluoromethylations carried out in CH_2Cl_2, or those in Et_2O to which phosphine was added after the formation of the $AgCF_3$ linkage, the only resonances found were near 47 ppm.

The almost identical chemical shifts measured for $AgCF_3(PPh_3)$ in CH_2Cl_2, 46.6 ppm, for $AgCF_3 \cdot OEt_2$ in ether, 46.3 ppm and for $AgCF_3(PMe_3)$, in CH_2Cl_2, 46.7 ppm, argue that in these relatively nonpolar solvents, the local chemical environment is nearly identical, as might be anticipated for species in which the silver ions were highly aggregated. Under these conditions, the $AgCF_3$ complexes are most probably tetrameric, as are $[AgI(PMe_3)]_4$ and $[AgI(PEt_3)]_4$ in the solid state [18].

The chemical shift differences found for $AgCF_3 \cdot$ glyme in glyme, 57.7 ppm [8], $AgCF_3(PPh_3)$ in glyme, 53.2 ppm, and $Ag(CF_3)_2^-$ in either glyme or ether, 51.7 ppm, indicate that these species are much more affected by chemical changes of both the solvent and the ligands, as would be expected from smaller aggregates.

Almost surely, $Ag(CF_3)_2^-$, at least, is monomeric. While in principle the states of aggregation, could be determined by an examination of the ^{31}P–Ag splitting patterns, as yet no coupling between the two nuclei has been observed at ambient temperature.

(Trifluoromethyl)silver(III) complex

By far the most thermally and photolytically stable of the $AgCF_3$ species observed in this study was that previously identified by Naumann [8] as the $Ag(CF_3)_4^-$ ion, an Ag^{III} complex that is indefinitely stable toward water and air. This product is readily formed when air is admitted to samples of any of the $AgCF_3$ phosphines discussed above, but it is not observed in the absence of added oxygen.

While the ^{19}F NMR data for $Ag(CF_3)_4^-$ and $AgCF_3(PMe_3)$ aggregates, cf. Tables 1 and 2, are very similar, the two types of compound can be easily distinguished by their behavior toward light, air, or water since $Ag(CF_3)_4^-$ is essentially unaffected by all three. Alternatively, the (presumably tetrameric) $AgCF_3$ phosphines are slightly soluble in pentane, whereas $Ag(CF_3)_4^-$ is not.

(Trifluoromethyl)copper(I) complexes

The ^{19}F NMR data clearly demonstrate that within 5 min $Cd(CF_3)_2 \cdot$ glyme reacts with CuBr to generate $CuCF_3$ complexes in high yields. Once formed, however, the Cu^ICF_3 species are less stable than the analogous silver complexes and at ambient temperature they completely decompose within 11 h. When PMe_3 was added to the $CuCF_3$ containing solutions, the decomposition, though retarded was not eliminated, and $CuCF_3(PMe_3)$ could not be isolated. The relative stabilities of the trifluoromethyl(trimethylphosphine) group 11 complexes are thus in the order Au > Ag > Cu.

In this study, in which air was rigorously excluded from the reaction, no indication for the most stable of the previously reported $CuCF_3$ complexes (Burton's C), $\delta \approx 43$ ppm [9], was obtained.

Summary

(Trifluoromethyl)group 11 derivatives are readily formed from the reactions of appropriate halides and acetates with $Cd(CF_3)_2 \cdot$ glyme. However, the ease with which these species can be handled decreases dramatically as the group is ascended, thus, while $AuCF_3(PMe_3)$ was readily synthesized and isolated, $CuCF_3(PMe_3)$, which is also readily formed, was not isolated. Oxidation of $AuCF_3(PMe_3)$ with the relatively weak oxidizing agent CF_3I provides an efficient entry into trifluoromethylgold(III) complexes. Although further studies will be required to completely delineate the reactivity of these systems, trifluoromethyl transfer reactions into which copper and silver ions have been introduced have already been shown to be significantly more effective than those in which the group 11 salts were omitted [2,9] which may be an early indication that the less stable Ag and Cu trifluoromethyl species will eventually prove to be as efficacious for the synthesis of perfluoroalkyl containing compounds as have their (also relatively unstable) perhydrogenated analogs for the synthesis of perhydroalkyl organic and inorganic compounds.

Acknowledgement

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References and notes

1 L.J. Krause, J.A. Morrison, J. Chem. Soc. Chem. Commun., (1980) 671; J. Am. Chem. Soc., 103 (1981) 2995; J. Chem. Soc. Chem. Commun., (1981) 1282; C.D. Ontiveros, J.A. Morrison. Organometallics, 5 (1986) 1446; E.J. Ganja, C.D. Ontiveros, J.A. Morrison, Inorg. Chem., 27 (1988) 4535; H.K. Nair, J.A. Morrison, ibid., 28 (1989) 2816.

2 J.A. Morrison, E.A. Ganja, 3rd Chem. Congr. North America, Toronto, June, 1988, Abstr. FLUO-29; J. Morrison, E. Ganja, D. Loizou, H. Nair, 12th Intern. Symp. Fluorine Chem., Santa Cruz, Calif. Aug. 1988, Abstr. 428.

3 For examples in which trifluoromethyl copper complexes are postulated (but not isolated); see V.C.R. McLoughlin, J. Thrower, Tetrahedron, 25 (1969) 5921; Y. Kobayashi, I. Kumadaki, Tetrahedron Lett., (1969) 4095; Y. Kobayashi, I. Kumadaki, K. Yamamoto, J. Chem. Soc. Chem. Commun., (1977) 536; Y. Kobayashi, K. Yamamoto, I. Kumadaki, Tetrahedron Lett., (1979) 4071; N.V. Kondratenko, E.P. Vechirko, L.M. Yagupolskii, Synthesis, (1980) 932; J. Leroy, M. Rubinstein, C. Wakselman, J. Fluorine Chem., 27 (1985) 291.

4 A. Johnson, R.J. Puddephatt, J. Chem. Soc. Dalton Trans., (1976) 1360.

5 M.A. Guerra, T.R. Biershenk, R.J. Lagow, J. Organomet. Chem., 307 (1986) C58.

6 H.H. Murray, J.P. Fackler, L.C. Porter, D.A. Briggs, M.A. Guerra, R.J. Lagow, Inorg. Chem. 26 (1987) 357.

7 K.J. Klabunde, J. Fluorine Chem., 7 (1976) 95.

8 W. Dukat, D. Naumann, Rev. Chim. Minerale, 23 (1986) 589. See also R.R. Burch, J.C. Calabrese, J. Am. Chem. Soc., 108 (1986) 5359.

9 D.M. Wiemers, D.J. Burton, J. Am. Chem. Soc., 108 (1986) 832.

10 C.D. Ontiveros, J.A. Morrison, Inorg. Synth., 24 (1986) 55.

11 F.G. Mann, D. Purdie, J. Chem. Soc. (1940) 1235.

12 R.A. Stein, C. Knobler, Inorg. Chem., 16 (1977) 242.

13 Fluorine-19 NMR data for *cis*-AuBr(CF$_3$)$_2$(PEt$_3$) δ 48.5 (dq), J(P–F) 73 Hz, J(F–F) 9 Hz (CF$_3$ *trans* to (PEt$_3$), δ 54.3 (apparent quintet), J(P–F) 10 Hz (CF$_3$ *cis* to PEt$_3$). As expected, the halide ligands *trans* to the phosphine are more labile than those *cis* to the phosphine, thus the first product of the trifluoromethylation of AuBr$_3$(PEt$_3$) is predominantly *trans*-AuBr$_2$(CF$_3$)(PEt$_3$).

14 Fluorine NMR data indicate that the yield of Au(CF$_3$)$_3$(PMe$_3$) from the reaction of AuI(CF$_3$)$_2$(PMe$_3$), 45 mg, with Cd(CF$_3$)$_2$·glyme, 100 mg, in CH$_2$Cl$_2$ can be readily increased to 70% by the addition of a 10 fold excess of CF$_3$I. In this reaction Le Chatelier's principle is utilized to drive reaction 5 toward the right thus retaining the gold substrate in the trivalent oxidation state during the extended period (10 days) that is required for the trifluoromethyl for halide interchange to occur at the "substitutionally inert" gold(III) center.

$$\mathrm{AuCF_3(PMe_3) + CF_3I \rightarrow AuI(CF_3)_2(PMe_3)} \qquad (5)$$

$$\mathrm{AuI(CF_3)_2(PMe_3) + Cd(CF_3)_2\cdot glyme \rightarrow Au(CF_3)_3(PMe_3)} \qquad (6)$$

15 The "coordination chemicals shifts", $\Delta\delta(^{31}P) = \delta(^{31}P)$(complexed phosphine) − $\delta(^{31}P)$(free phosphine), are commonly taken as measures of the combined electronic and steric effects resulting from the coordination of the phosphine to the metal. In the dicoordinate gold(I) complexes considered here, it seems unlikely that significant geometrical changes would be sterically forced upon the phosphine by coordination. See, for example, C.A. Tolman, Chem. Rev., 77 (1977) 313; A.R. Barron, J. Chem. Soc. Dalton Trans., (1988) 3047; M.M. Rahman, H. Liu, K. Eriks, A. Prock, W.P. Giering, Organometallics, 8 (1989) 1.

16 Kochi has reported the formation of Au(CH$_3$)$_3$(PPh$_3$) from a similar ligand interchange between AuI(CH$_3$)$_2$(PPh$_3$) and AuCH$_3$(PPh$_3$). A. Tamaki, J.K. Kochi, J. Organomet. Chem. 40 (1972) C81. Also see ref. 4.

17 For example, in acetone Au(CF$_3$)$_3$(PEt$_3$) slowly generates a derivative with the following ^{19}F spectrum: δ 52.7 (q) ppm, J(F–F) 7 Hz (6F); δ 47.0 (h) ppm, J(F–F) 7 Hz (3F). These resonances

are currently ascribed to $Au(CF_3)_3$·acetone, the structure of which, like the rest of the gold(III) species discussed here, would be expected to be based upon square planar geometry. In a variety of reactions such as the trifluoromethylation of $AuBr_3(PEt_3)$, an intense resonance was observed at 43.2 (s) ppm. Our current evidence suggests that this resonance is derived from $Au(CF_3)_4^-$. Similarly facile displacements of Lewis bases by $C_6F_5^-$ are reported in ref. 6 and in R. Uson et al., J. Chem. Soc. Dalton Trans., (1982) 1971.

18 M.R. Churchill, B.G. De Boer, Inorg. Chem. 14 (1975) 2502; See also B.K. Teo, J.C. Calabrese, J. Am. Chem. Soc., 97 (1975) 1256.

19 Abstracted from the Ph.D. Thesis of H.K. Nair, University of Illinois at Chicago, 1987.