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Polar trifluoromethylation reactions: syntheses of trifluoromethyl gallium, indium, and thallium compounds. The mechanism of polar trifluoromethyl group transfer *

Dieter Naumann *, Werner Strauß [1] and Wieland Tyrra

Institut für Anorganische Chemie, Universität zu Köln, Greinstr. 6, W-5000 Köln 41 (Germany)

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Abstract

The reactions of $Cd(CF_3)_2$ complexes with $GaCl_3$, $InCl_3$, and TlX_3 (X: Cl, $OCOCH_3$, $OCOCF_3$) in aprotic basic solvents have given the compounds $Ga(CF_3)_3 \cdot dmf$, $Ga(CF_3)_2Cl \cdot dmf$, $[Cd(CH_3CN)_2][Ga(CF_3)_4]_2$, $In(CF_3)_3 \cdot 2CH_3CN$, $In(CF_3)_2Cl \cdot dmf$, and $Tl(CF_3)_3 \cdot 2dmf$, which have been characterized by NMR spectroscopy, mass spectrometry, vibrational spectroscopy, and elemental analysis. All trifluoromethylmetal halides formed as intermediates were detected by ^{19}F NMR spectroscopy. The dependence of the chemical shifts and the coupling constants $^2J(^{203/205}Tl-^{19}F)$ on the number of CF_3-groups bound to the central atom provides unambiguous evidence for the formular of trifluoromethyl gallates and thallates and the existence of the $[Ga(CF_3)_4]^-$-anion has been confirmed by ^{71}Ga NMR spectroscopy.

A mechanism for successful polar trifluoromethyl group transfer is discussed on the basis of Pearson's HSAB concept and the results of conductivity measurements.

Introduction

Pentafluorophenyl derivatives of Main Group III elements are well known, but there are only a few reports of trifluoromethyl compounds. The C_6F_5-derivatives can be synthesized readily by the "classical" halide aryl exchange reactions involving lithium, magnesium, or mercury compounds [2]. Although trifluoromethylboron compounds are well-established [3] there has until now been only weak evidence for the formation of CF_3-derivatives of aluminium and gallium [4,5]. However, trifluoromethyl-indium and -thallium derivatives were prepared in low yields by Lagow and co-workers from the reactions of CF_3-radicals with the corresponding metal vapour [5,6] and Morrison and Nair [7] reported the syntheses of $C_6H_5Tl(CF_3)_2$ and $Tl(CF_3)_2OCOCH_3$.

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[1] Present address: Schering A.G., Bergkamen, Germany.

Results and discussion

Mechanism

Bis(trifluoromethyl)cadmium complexes have been shown to be effective Grignard reagent analogues [8]. Successful halide-trifluoromethyl exchange reactions involving these compounds have given some new or only difficultly available trifluoromethyl element compounds. The results of our studies on polar halide trifluoromethyl group exchange reactions enable us to propose an improved mechanism [9] for the synthesis of CF_3-element compounds.

An explanation for the features of these reactions can be given in terms of Pearson's HSAB concept [10]. In a polar trifluoromethyl group transfer the CF_3-group must be considered to be a softer base than a halide ion. Stable compounds are formed if the "soft" base is allowed to react with a "soft" acid. Solvent influences are thus significant; solvent molecules reversibly coordinated to cationic centers lower the hardness of the cation, and the formation of a stable σ-bond between the CF_3-group and the cationic center is favoured.

We assume the following reaction sequence:

$$Cd(CF_3)_2 \rightleftharpoons [Cd(CF_3)]^+ + \underset{(\text{“soft” base})}{\langle CF_3^- \rangle}$$

$$MX_n \cdot D \rightleftharpoons X^- + \underset{(\text{“soft” acid})}{[MX_{n-1} \cdot D]^+}$$

$$[MX_{n-1} \cdot D]^+ + \langle CF_3^- \rangle \rightleftharpoons MX_{n-1}(CF_3) + D$$

(M: e.g. metal atom, X: e.g. halide; D: solvent with donor properties; donor molecules complexed with $Cd(CF_3)_2$ are omitted)

The dissociation of $Cd(CF_3)$-complexes in solvents with donor properties was indicated by conductivity measurements of the corresponding $Cd(n\text{-}C_6F_{13})$- and $Cd(n\text{-}C_8F_{17})$-complexes [11]. The molar conductivity of these complexes in dmf is comparable to that of KCl in water at 25 °C. The most important properties a suitable solvent should possess are (i) inertness towards the trifluoromethyl cadmium compounds, (ii) a high dielectric constant to induce dissociation of the starting materials, usually halides or trifluoroacetates, and (iii) donor properties to reduce the hardness of the cationic Lewis-acid.

Finally conditions have to be adopted that allow rapid combination of the acid with the base $\langle CF_3^- \rangle$ to form a stable σ-bond. Otherwise a decomposition of the CF_3 group is favoured, yielding difluorocarbene and fluoride ion.

Applying this mechanistic concept in our investigations on Main Group III compounds we found that acetonitrile is a particularly suitable solvent for polar trifluoromethylation reactions with gallium and indium trihalides, whereas dmf is suitable for reactions with thallium salts.

Conductivity measurements were carried out in order to check which system is the most suitable. Table 1 lists the conductivity data for $InCl_3$ in CH_2Cl_2, CH_3CN, and dmf and reveals that solvated $InCl_3$ is dissociated. Thus the required soft cationic intermediate for polar trifluoromethylation is formed.

Table 1

Molar conductivity of $InCl_3$ in various solvents at 24° C

Solvent	Λ (Ω^{-1} cm^2 mol^{-1})	c (mol cm^{-3})
CH_2Cl_2	0.074	$3.03 \cdot 10^{-3}$
dmf	1.475	$3.93 \cdot 10^{-6}$
CH_3CN	49.967	$1.98 \cdot 10^{-6}$
CH_2Cl_2 + dmf	127.178	$1.81 \cdot 10^{-8}$

The reactions with gallium trichloride

Reactions of $Cd(CF_3)_2 \cdot D$ and $GaCl_3$ in a molar ratio of 3 : 2 in solvents such as dmf or CH_3CN do not proceed very selectively. The trifluoromethyl gallium compounds $Ga(CF_3)_3$, $Ga(CF_3)_2Cl$, and $Ga(CF_3)Cl_2$ can be detected by ^{19}F NMR spectroscopy. A typical ^{19}F NMR spectrum is given in Fig. 1. The singlets at δ -50.95 ppm, δ -53.72 ppm, and δ -56.14 ppm can be assigned to $Ga(CF_3)_3 \cdot$ dmf, $Ga(CF_3)_2Cl \cdot$ dmf, and $Ga(CF_3)Cl_2 \cdot$ dmf, respectively. The multiplet at δ -47.77 ppm is to be assigned to $[Ga(CF_3)_4]^-$. If, as we assume, the most probable spherical arrangement of the gallate is tetrahedral, then the quadrupole relaxation effect is lowered. Thus the spin–spin-interaction of the ^{19}F nuclei with the ^{69}Ga and ^{71}Ga nuclei should split the resonance into two four-line multiplets in accord with the gallium nuclear spins of three-halves.

The $^2J(^{69/71}Ga-^{19}F)$ couplings in the ^{19}F NMR spectrum are 150.2 and 189.0 Hz, respectively. The presence of the $[Ga(CF_3)_4]^-$ is confirmed by the ^{71}Ga NMR spectrum (Fig. 2), which shows 9 lines of the tridecet centered at δ $+170.90$ ppm upfield from $[Ga(H_2O)_6]^+$ with a $^2J(^{71}Ga-^{19}F)$ coupling of 189 Hz. The intensity ratio of the inner lines indicates a tridecet due to Pascal's triangle.

Increase in the molar ratio of $GaCl_3$ to $Cd(CF_3)_2 \cdot 2CH_3CN$ in CH_3CN to 1 : 5 leads to formation of $[Ga(CF_3)_4]^-$ as the only gallium-containing product. This compound is a further example of fully trifluoromethylated metallates like $[Cd(CF_3)_4]^{2-}$ [12] and $[Ag(CF_3)_4]^-$ [13].

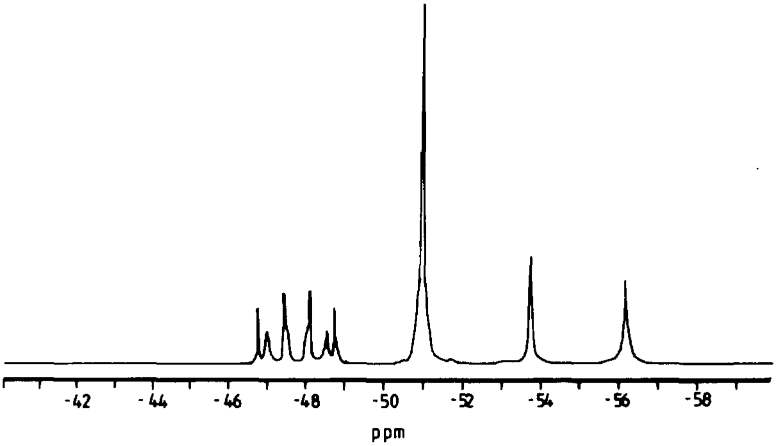

Fig. 1. ^{19}F NMR spectrum of the trifluoromethyl gallium compounds formed during the reaction of $GaCl_3$ with $Cd(CF_3)_2 \cdot$ glyme in dmf.

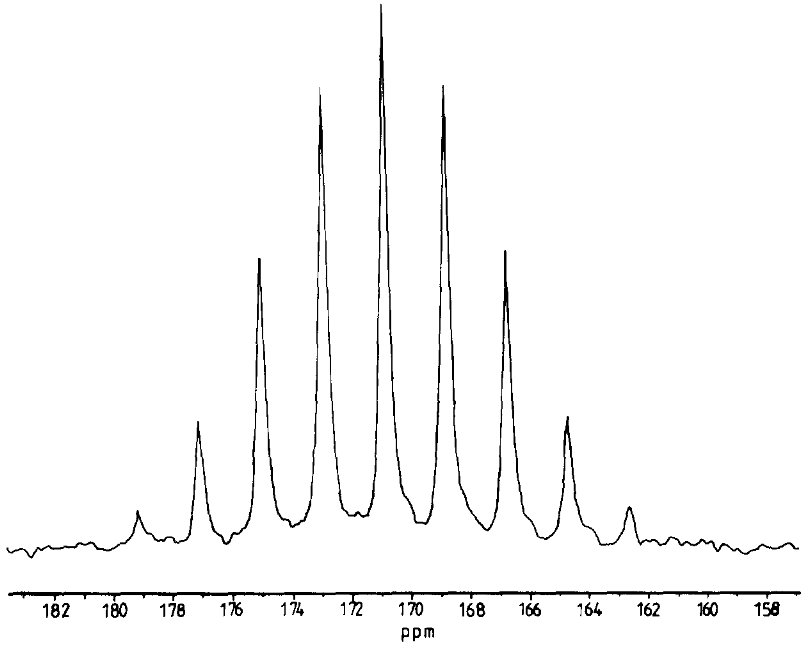

Fig. 2. ^{71}Ga NMR spectrum of $[Ga(CF_3)_4]^-$.

The assignment of the $Ga(CF_3)_3$-resonance is unambiguous. The singlet at δ – 50.95 ppm is surrounded by ^{13}C satellites split into septets ($^1J(^{19}F-^{13}C)$ 341.9 Hz, $^4J(^{19}F-^{19}F)$ 4.1 Hz, $^1\Delta(^{19}F-^{12/13}C)$ 0.1400 ppm).

The careful examination of the ^{13}C satellites of trifluoromethyl element compounds allows unambiguous determination of the number of CF_3-groups bound to a central atom [14]. The ^{13}C satellites must be assigned to the $^{13}CF_3$-group of $Ga(^{12}CF_3)_2(^{13}CF_3) \cdot$ dmf. The resonance of the corresponding $^{12}CF_3$-groups is superposed on the signal of $Ga(^{12}CF_3)_3 \cdot$ dmf. The splitting of the satellites into septets results from the spin–spin-interaction of the fluorine atoms of the $^{13}CF_3$-group with six fluorine atoms of the two $^{12}CF_3$-groups. The assignment of the signals at δ –53.72 ppm and δ –56.14 ppm can be made by analogy with previous results. Partly-halogenated trifluoromethyl element compounds generally show a significant upfield shift compared with fully trifluoromethylated compounds (Table 2).

Gallium trichloride is soluble in many chlorohydrocarbons. With methyl chloride 1 : 1 and 1 : 2 adducts are formed, and are stable up to 10 °C [18]. No dissociation into cationic and anionic gallium derivatives is observed. In contrast ether, nitrile, and amine adducts dissociate according to the following equation [19]:

$$2\ GaCl_3 \cdot D \rightleftharpoons [GaCl_2 \cdot D_2]^+ + [GaCl_4]^-$$

Because many by-products were formed during the reactions in polar solvents, especially CH_3CN, we used CH_2Cl_2 as the solvent and dmf as the complexing agent. The reaction in a molar ratio $GaCl_3/Cd(CF_3)_2$ of 1 : 1 yielded $Ga(CF_3)_2Cl \cdot$ dmf ($\delta(^{19}F)$ –52.60 ppm) as the main product; an approximately three-fold excess of $Cd(CF_3)_2 \cdot 2CH_3CN$ favoured the formation of $Ga(CF_3)_3 \cdot$ dmf ($\delta(^{19}F)$ –50.95 ppm). Both compounds were isolated, and identified from their NMR and mass spectra and elemental analysis.

Table 2

Changes in the ^{19}F NMR chemical shifts of trifluoromethyl derivatives of Main Group elements, $E(CF_3)_{3-n}X_n$ and $E(CF_3)_{4-m}X_m$ (X: Cl, Br; n: 0–2; m: 0–3), upon variation of the number of CF_3 groups on the central atom

E	X	$m, n = 0$ δ (ppm)	$m, n = 1$ δ (ppm)	$m, n = 2$ δ (ppm)	$m = 3$ δ (ppm)	Ref.
Ga	Cl	−50.95	−53.72	−56.14		
P	Cl	−50.7	−63.3	−72.8		[15]
Sb	Cl, Br	−41.2	−52.3	−60.4		[9]
Bi	Cl	−33.4	−37.8	−40.2		[8]
Ge	Br	−50.9	−55.4	−59.4	−65.2	[16]
Sn	Br	−39.7	−42.2	−43.8	−47.7	[16,17]

It is well-known that organogallium derivatives usually prefer a 1 : 1 coordination with N, O, and P donors [2]. In contrast to the extremely moisture- and air-sensitive triorganogallium derivatives, the mono- and di-organo compounds are not hydrolysable and are resistant to oxidation reactions [20]. Redistribution equilibria between triorganogallium compounds and trihalides lead to formation of diorganogallium monohalides, e.g. [21]:

$$2\,Ga(CH_3)_3 + GaCl_3 \xrightarrow{Et_2O} 3\,Ga(CH_3)_2Cl \cdot OEt_2$$

We assume that $Ga(CF_3)_2Cl$ and $Ga(CF_3)_3$ are formed as 1:1 adducts with dmf because the gallium-containing fragments in the mass spectra are consistent with such adducts.

It is noteworthy that $Ga(CF_3)_2Cl \cdot dmf$ is soluble in water as well as in toluene with significant changes in the ^{19}F NMR chemical shift (by ca. 1.5 ppm) and coupling constant $^1J(^{19}F-^{13}C)$ (by 2.5 Hz). That indicates the presence of two different species in these solutions. After removal of the solvent $Ga(CF_3)_2Cl \cdot dmf$ can be recovered unchanged. This behaviour indicates that the gallium compound may be reversibly complexed with H_2O:

$$Ga(CF_3)_2Cl \cdot dmf \underset{-H_2O}{\overset{+H_2O}{\rightleftharpoons}} [Ga(CF_3)_2 \cdot dmf \cdot H_2O]^+ + Cl^-$$

whereas in toluene the complex is molecularly solvated.

The reactions with indium trichloride

In polar solvents trifluoromethyl cadmium compounds react with indium trichloride primarily by trifluoromethyl-chlorine exchange.

$$Cd(CF_3)_2 + InCl_3 \xrightarrow{D} In(CF_3)_{3-x}Cl_x \cdot D + CdCl_2$$

(x: 0–2; D: dmso, thf, CH_3CN, dmf, pyridine; complexation equilibria of $Cd(CF_3)_2 \cdot 2D$ are generally neglected)

$In(CF_3)_3 \cdot D$, $In(CF_3)_2Cl \cdot D$ and $In(CF_3)Cl_2 \cdot D$ are identified from their ^{19}F NMR spectra. In all the spectra the $In(CF_3)_2Cl \cdot D$ resonance gives the most intense signal.

The ^{19}F NMR data for trifluoromethyl indium compounds are listed in Table 3.

Table 3

^{19}F NMR spectroscopic data [a] for $In(CF_3)_{3-x}Cl_x \cdot D$ (x: 0–2) in several solvents

x	D (δ (ppm))				
	dmso	thf	CH_3CN	dmf	pyridine
0	−41.63	−40.65 [b]	−44.46	−44.90	−39.06
1	−44.78	−42.75 [c]	−45.55	−46.15	−40.25 [d]
2	−46.49	−43.40	−46.71	−47.25	−41.41

[a] cp. $In(CF_3)_3$ (CD_2Cl_2) δ −42.5 ppm, $In(CF_3)_3 \cdot PMe_3$ δ −41.7 ppm [6]. [b] $^1J(^{19}F-^{13}C)$ 360.1 Hz, $^1\Delta(^{19}F-^{12/13}C)$ 0.1333 ppm. [c] $^1J(^{19}F-^{13}C)$ 360.0 Hz. [d] $^1J(^{19}F-^{13}C)$ 367.1 Hz, $^1\Delta(^{19}F-^{12/13}C)$ 0.1369 ppm.

The chemical shifts for the trifluoromethyl indium compounds depend strongly on the solvent. This shows that the indium compounds form solvent adducts, but gives no indication of whether 1 : 1 adducts or 1 : 2 adducts are formed. It is known that indium trihalides [22] and pentafluorophenyl indium derivatives [23] form stable 1 : 2 adducts with donor solvents; if we regard perfluorinated organic groups as pseudohalides we can assume that the CF_3-compounds can also in principle form 1 : 2 adducts, but 1 : 1 adducts are the usual complexes in the case of organoindium derivatives [2].

In solvents such as acetonitrile, dmf, or pyridine the exchange reactions proceed without the formation of any fluorinated by-products.

In the case of reactions in acetonitrile or dichloromethane-dmf mixtures we were able to obtain $In(CF_3)_3 \cdot 2CH_3CN$ and $In(CF_3)_2Cl \cdot dmf$ selectively by varying the stoichiometry of the starting materials. Both compounds are stable white to yellow solids that decompose at ca. 80 °C. The reaction in CH_3CN in the presence of PPh_3 provides evidence for the formation of a difluoromethyl phosphonium salt [24]. The reaction between $InCl_3$ and $Cd(CF_3)_2 \cdot 2CH_3CN$ in dmso initially proceeds straightforwardly; a subsequent Cl–CF_3-exchange at the indium atom and a CF_3–Cl-exchange at the cadmium atom can be detected by ^{19}F NMR spectroscopy. The changes in the values of the $^2J(^{111/113}Cd-^{19}F)$ coupling constants indicate complexation of the cadmium compounds with dmso.

$$Cd(CF_3)_2 \cdot 2CH_3CN + 2(CH_3)_2SO \rightarrow Cd(CF_3)_2 \cdot 2(CH_3)_2SO + 2CH_3CN$$

$$Cd(CF_3)_2 \cdot 2(CH_3)_2SO + InCl_3$$
$$\rightarrow Cd(CF_3)Cl \cdot 2(CH_3)_2SO + CdCl_2 \cdot 2(CH_3)_2SO + In(CF_3)_{3-x}Cl_x \cdot (CH_3)_2SO$$

(x: 0–2)

Figure 3 shows the ^{19}F NMR spectra of the reaction mixture recorded after 1 day (a), 7 days (b), and 21 days (c). It can be seen that a prolongation of the reaction leads to formation of further trifluoromethyl indium compounds, and this is accompanied by formation of $(CF_3)_2SO$. The outcome of the reaction pathway implies that $In(CF_3)$-compounds undergo CH_3–CF_3-exchange reactions with the sulfoxide:

$$In(CF_3)_{3-x}Cl_x + (CH_3)_2SO \rightarrow In(CF_3)_{3-x-y}(CH_3)_yCl_x + (CF_3)_2SO$$

($x + y \leq 3$, x: 0–2, y: 1–3)

As expected, seven $In(CF_3)$-compounds can be detected in the ^{19}F NMR spectra.

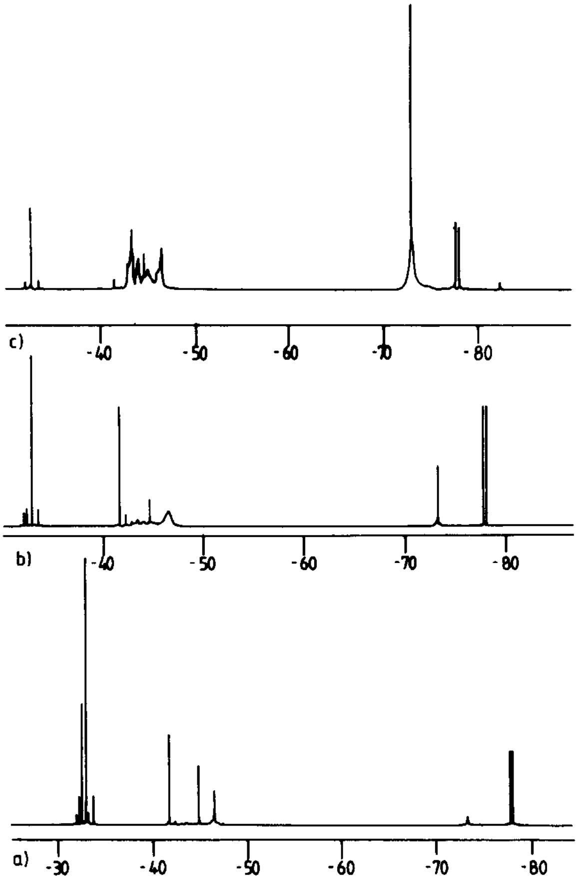

Fig. 3. ^{19}F NMR spectra of a reaction mixture of $InCl_3$ and $Cd(CF_3)_2 \cdot 2CH_3CN$ in dmso, (a) after 1 day; (b) after 7 days; (c) after 21 days.

The reactions with thallium trichloride, triacetate, and tris(trifluoroacetate)

Bis(trifluoromethyl)cadmium complexes react in basic complexing solvents such as CH_3CN, dmf, and pyridine with TlX_3 (X: Cl, $OCOCH_3$, $OCOCF_3$) to form the corresponding tris(trifluoromethyl)thallium complexes:

$$2TlX_3 + 3Cd(CF_3)_2 \xrightarrow{D} 2Tl(CF_3)_3 \cdot 2D + 3CdX_2$$

(D: pyridine, dmf, dmso, CH_3CN)

From these reactions $Tl(CF_3)_3 \cdot 2$dmf, $Tl(CF_3)_3 \cdot 2$dmso, and $Tl(CF_3)_3 \cdot 2$py have been isolated as stable products and fully characterized. $Tl(CF_3)_3 \cdot 2$dmf was isolated from the reaction in dmf. The dmso and pyridine adducts are formed in separate complexation reactions from $Tl(CF_3)_3 \cdot 2$dmf (Table 4).

The ^{19}F NMR spectra (Fig. 4) show a typical pattern for thallium compounds. The resonance of $Tl(CF_3)_3$ is split into two doublets due to $^2J(^{203}Tl-^{19}F)$ and $^2J(^{205}Tl-^{19}F)$ couplings. An unambiguous assignment of the resonances can be made by analysis of the splitting of the ^{13}C satellites. The septets of the ^{13}C satellites indicate that the thallium atom is surrounded by three magnetically-equivalent

Table 4

^{19}F NMR data for the tris(trifluoromethyl)thallium complexes

	$\delta(^{19}F)$ (ppm)	$^{2}J(^{203/205}Tl-^{19}F)$ (Hz)
$Tl(CF_3)_3 \cdot 2dmf$	−36.8	3010/3040
$Tl(CF_3)_3 \cdot 2py$	−35.16	2940/2970
$Tl(CF_3)_3 \cdot 2dmso$	−36.05	2978/3006

CF_3-groups (Fig. 4). The ^{13}C NMR spectrum shows two doublets ($^{1}J(^{203/205}Tl-^{13}C)$) of quartets ($^{1}J(^{19}F-^{13}C)$) of septets ($^{3}J(^{19}F-^{13}C)$). The coupling constants are 7802, 382, and 13 Hz, respectively (Table 5).

In order to study the acceptor properties of $Tl(CF_3)_3 \cdot 2D$ we made several attempts to obtain trifluoromethyl thallates. Although a large number of pentafluorophenylhalogeno thallates are known [25], we did not find any evidence for formation of trifluoromethylhalogeno thallates from reactions with cesium halides. However, the reaction of $Tl(CF_3)_3 \cdot 2D$ with $Cd(CF_3)_2 \cdot$ glyme in dmf at 45 °C did give several trifluoromethyl thallates. Similar products are also formed upon treatment of $TlCl_3$ with a large excess of $Cd(CF_3)_2 \cdot D$. Comparison of the hetero atom–fluorine coupling constants of the trifluoromethyl thallium, cadmium, and silver compounds as well as the thallium–hydrogen coupling constants of methyl thallium compounds shows that in all cases the absolute values of the hetero atom–fluorine or -hydrogen coupling constants fall with increase in the number of CF_3- or CH_3-groups bound to the central atoms (Table 6). If this effect is general for trifluoromethyl metallates we can assume that $[Tl(CF_3)_4]^{-}$, $[Tl(CF_3)_5]^{2-}$, and $[Tl(CF_3)_6]^{3-}$ may have been formed during this reaction. The results do not give any indication of the coordination number of the thallium compounds. Although

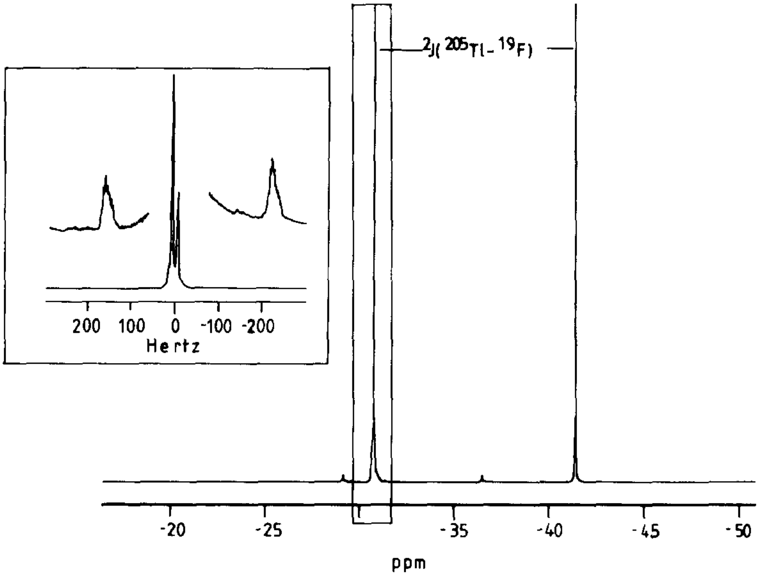

Fig. 4. ^{19}F NMR spectrum of $Tl(CF_3)_3 \cdot 2dmso$.

Table 5

^{13}C NMR data for trifluoromethyl element compounds of the 6th period

	Solvent	δ (CF$_3$) (ppm)	$^1J(^{19}F-^{13}C)$ (Hz)	$^3J(^{19}F-^{13}C)$ (Hz)	$^1J(^xE-^{13}C)$ (Hz)
$Tl(CF_3)_3 \cdot 2dmso$ [a]	CD_3CN	168.27	382	13	^{205}Tl: 7802
$Hg(CF_3)_2$	thf	160.00	355	16	^{199}Hg: 2866
$Bi(CF_3)_3$ [b]	neat	189.80	391	[c]	

[a] δ(dmso) +40.15 ppm. [b] Ref. 8. [c] Not resolved.

the usual coordination number of thallium is five, four- and six-coordinated species are known, and so it is possible that e.g., $[Tl(CF_3)_4]^-$ is coordinated by one or two solvent molecules.

The formation of the thallates seems to be temperature dependent. At room temperature $[Tl(CF_3)_4]^-$ is mainly formed. Raising the temperature to 45–60 °C leads to formation of $[Tl(CF_3)_5]^{2-}$ and $[Tl(CF_3)_6]^{3-}$. Cooling to room temperature leads to the formation of $[Tl(CF_3)_4]^-$.

$$Cd(CF_3)_2 \cdot glyme + Tl(CF_3)_3 \cdot 2dmso \xrightarrow{r.t.} [Tl(CF_3)_4]^- + Cd(CF_3)^+ + glyme + 2dmso$$

$$11[Tl(CF_3)_4]^- \underset{r.t.}{\overset{45-60\,°C}{\rightleftharpoons}} 4[Tl(CF_3)_5]^{2-} + 4[Tl(CF_3)_6]^{3-} + 3\,Tl^{3+}$$

Although none of the thallates was isolated the ^{19}F NMR spectra of the thallium compounds make it possible to define the behaviour of $Tl(CF_3)_3 \cdot 2D$ in the reactions. A critical comparison of the ^{19}F NMR data, especially the coupling constants, shows that identification of new compounds solely on the bases of NMR data is not limited to Cd(CF$_3$)- and Ag(CF$_3$)-compounds.

Table 6

Dependence of the coupling constants for methyl [26] and trifluoromethyl element compounds [12] on the number of methyl or trifluoromethyl groups bound to the central atom

	$^2J(^{205}Tl-^1H)$ (Hz)	solvent		$^2J(^{205}Tl-^{19}F)$ (Hz)
$CH_3Tl(OCOCH_3)_2$	911	CH_3CN	$Tl(CF_3)Cl_2$	5068
$(CH_3)_2TlOClO_3$	412	CH_3CN	$Tl(CF_3)_2Cl$	3358
$(CH_3)_3Tl$	266	glyme	$Tl(CF_3)_3 \cdot 2dmso$	3006
$Li[Tl(CH_3)_4]$	221	glyme	$[Tl(CF_3)_4]^-$	2072
			"$[Tl(CF_3)_5]^{2-}$"	1880
			"$[Tl(CF_3)_6]^{3-}$"	1420
	$^2J(^{113}Cd-^{19}F)$ (Hz)			$^2J(^{109}Ag-^{19}F)$ (Hz)
$CdCF_3^+$	559		$AgCF_3 \cdot glyme$	129
$Cd(CF_3)I \cdot glyme$	501			
$Cd(CF_3)_2 \cdot glyme$	469		$[Ag(CF_3)_2]^-$	101
$[Cd(CF_3)_2I \cdot glyme]^-$	416			
$[Cd(CF_3)_3 \cdot glyme]^-$	281		$Ag(CF_3)_3 \cdot CH_3CN$ [a]	91.6
			$[Ag(CF_3)_3Cl]^-$ [a]	72.4
$[Cd(CF_3)_4]^{2-}$	199		$[Ag(CF_3)_4]^-$	40.7

[a] *trans*-Couplings.

Experimental

NMR spectra. Bruker FT NMR spectrometers AM 300 and WM 300; ^{19}F NMR: 282.4 MHz, ^{13}C NMR: 75.6 MHz, ^{71}Ga NMR: 91.5 MHz; Standards CCl_3F (ext., ^{19}F), TMS (ext., ^{13}C); 1 *M* $Ga(NO_3)_3/D_2O$(ext., ^{71}Ga).

Vibrational spectra. IR spectra: Perkin-Elmer spectrograph PE 580 B; Raman spectra: Coderg Model PHO, and exciter Spectra Physics (Kr Laser, λ_0 488 nm).

Mass spectra. MAT Finnigan 8230 and Varian MAT CH5.

Molecular weight determinations. Knauer vapour pressure osmometer.

Elemental analysis. C, H, N: Heraeus Typ CHN Micro; Cd, Ga, In: acc. to ref. 28*. Cl: acc to ref. 27.

Preparations. All reactions were carried out under dry nitrogen. Solvents and all other compounds were purified by standard methods. $Cd(CF_3)_2$ complexes were prepared as previously described [29].

General procedure for the preparation of trifluoromethyl Main Group III compounds

The metal chloride was dissolved or suspended in the appropriate solvent at room temperature or below. The complexing ligand and the $Cd(CF_3)_2$ complex were added with vigorous stirring. The completion of the reaction was determined by ^{19}F NMR spectroscopy. In reactions of $Cd(CF_3)_2$-ether complexes with $GaCl_3$ or $InCl_3$, difluoromethylethers and $CClF_2H$ were formed as by-products and identified from their NMR spectra [30]. The trifluoromethyl compounds were purified by repeated extraction with CH_2Cl_2 (Ga, In) or recrystallization from diethyl ether (Tl). Experimental details for the exchange reactions are given in Table 7, analytical data in Tables 8 and 9.

Mass spectra of Ga(CF_3)-compounds (only ^{69}Ga containing fragments)

$Ga(CF_3)_3 \cdot$ dmf (70 eV, 20 °C, *m/e*): 330 ($[Ga(CF_3)_2(CF_2) \cdot dmf]^+$, 0.3%); 280 ($[Ga(CF_3)_2 \cdot dmf]^+$, 2.6%); 230 ($[Ga(CF_3)F \cdot dmf]^+$, 4.3%); 180 ($[GaF_2 \cdot dmf]^+$, 5.5%).

$Ga(CF_3)_3 \cdot$ dmf (20 eV, 60 °C, *m/e*): 299 ($[Ga(CF_3)_2F \cdot dmf]^+$, 1.0%); 280 ($[Ga(CF_3)_2 \cdot dmf]^+$, 4.3%); 230 ($[Ga(CF_3)F \cdot dmf]^+$, 15.0%); 180 ($[GaF_2 \cdot dmf]^+$, 3.6%).

$Ga(CF_3)_2Cl \cdot$ dmf (70 eV, 20 °C, *m/e*): 280 ($[Ga(CF_3)_2 \cdot dmf]^+$, 9.9%); 230 ($[Ga(CF_3)F \cdot dmf]^+$, 18.4%); 180 ($[GaF_2 \cdot dmf]^+$, 22.1%); 69 ($^{69}Ga^+$ and $CF_3{}^+$, 5.5%).

To decide whether the peak at 69 *m/e* comes from $[^{69}Ga]^+$ or $[CF_3]^+$ the spectrum was enlarged. Two peaks were now detectable, at 69.01 *m/e*, 2.01% and 68.92 *m/e*, 3.36%, corresponding to $[CF_3]^+$ and $[^{69}Ga]^+$. Mass spectra recorded at 20 eV gave a similar fragmentation pattern. Peaks of highest intensity were in all cases 81 *m/e*, 100%, $[C_2F_3]^+$ and 50 *m/e*, ~ 70%, $[CF_2]^+$. Additional signals with masses between 70 and 45 *m/e* are fragments of dmf.

Vibrational spectra of the Tl(CF_3)$_3$-complexes

$Tl(CF_3)_3 \cdot$ 2dmf. Raman: 203 vs, 223 m, 408 w, 516 w, 675 w, 709 s, 867 m, 872 w, 1017 vw, 1065 vw, 1114 m, 1144 s, 1335 vw, 1390 vw, 1426 s, 1444 m, 1508 vw, 1661 w, 2956 m. IR (Nujol): 409 w, 708 w, 867 vw, 1070 vs,br, 1102 vs, 1143 s, 1258 m, 1422 m, 1442 s, 1498 w, 1654 vs, 2940 w.

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* A reference number with an asterisk indicates a note in the list of references.

Table 7

Exchange reactions of Main Group III chlorides with $Cd(CF_3)_2$ complexes

$Cd(CF_3)_2 \cdot D$ (mmol)	D	MX_3 (mmol)	Solvent (ml)	reaction temp.	reaction time	reaction products [a] (yield)
1.50	glyme	$GaCl_3$ (1.00)	CH_3CN (6)	−15 °C → r.t.	1d	$Ga(CF_3)_2Cl \cdot 2CH_3CN$, $Ga(CF_3)_3 \cdot 2CH_3CN$, $Ga(CF_3)Cl_2 \cdot 2CH_3CN$, $[Cd(CH_3CN)_2][Ga(CF_3)_4]_2$ [b]
5.68	diglyme	$GaCl_3$ (4.54)	CH_2Cl_2 (10) +dmf (0.35)	r.t. → −30 °C → r.t.	2d	$Ga(CF_3)_2Cl \cdot dmf$ (39%)
22.20	$2CH_3CN$	$GaCl_3$ (8.08)	CH_2Cl_2 (25) +dmf (0.63)	r.t. → −30 °C → r.t.	4d	$Ga(CF_3)_3 \cdot dmf$ (42%)
2.30	diglyme	$GaCl_3$ (1.48)	CH_2Cl_2 (2) +dmeu [c] (0.15)	r.t. → −30 °C → r.t.	2d	$Ga(CF_3)_2Cl \cdot dmeu$
6.02	$2CH_3CN$	$GaCl_3$ (1.20)	CH_3CN (10)	r.t.	7d	$[Cd(CH_3CN)_2][Ga(CF_3)_4]_2$ (49%)
15.00	$2CH_3CN$	$InCl_3$ (10.00)	CH_3CN (20)	r.t.	1d	$In(CF_3)_3 \cdot 2CH_3CN$ [d] (36%)
10.00	$2CH_3CN$	$InCl_3$ (10.00)	CH_2Cl_2 (20) +dmf (0.78)	reflux	3d	$In(CF_3)_2Cl \cdot dmf$ [e] (32%)
34.30	diglyme	$TlCl_3$ (19.90)	dmf (68)	r.t. → 40 °C	2d	$Tl(CF_3)_3 \cdot 2dmf$ (45%)

[a] The products were identified by ^{19}F NMR spectroscopy. [b] Similar results were obtained in dmf. [c] 1,3-Dimethyl-2-imidazolidinone. [d] $\delta(^{19}F)$ −44.03 ppm (CH_3CN); −42.54 ppm (Et_2O); −44.25 ppm (CH_2Cl_2). [e] $\delta(^{19}F)$ −45.81 ppm (CH_2Cl_2). Although the ^{19}F NMR spectrum of the reaction mixture showed the signals from $In(CF_3)_3 \cdot dmf$, $In(CF_3)_2Cl \cdot dmf$, and $In(CF_3)Cl_2 \cdot dmf$ in a ratio of 1.0:5.5:1.3 we could only isolate $In(CF_3)_2Cl \cdot dmf$; we thus assume that there is a distribution equilibrium $In(CF_3)_3 \cdot dmf + In(CF_3)Cl_2 \cdot dmf \rightleftharpoons 2In(CF_3)_2Cl \cdot dmf$.

Table 8

Elemental analyses for trifluoromethyl gallium and indium derivatives

Compound	Elemental analysis (%)	
	Ga or In Found (calc.)	Cl or Cd Found (calc.)
$Ga(CF_3)_3 \cdot dmf$	19.20 (19.93)	1.30 (0)
$Ga(CF_3)_2Cl \cdot dmf$	21.90 (22.05)	11.89 (11.21)
$Cd(CH_3CN)_2[Ga(CF_3)_4]_2$	15.55 (15.57)	12.61 (12.68)
$In(CF_3)_3 \cdot 2CH_3CN$	28.58 (28.43)	2.23 (0)
$In(CF_3)_2Cl \cdot dmf$	32.32 (31.78)	9.50 (9.81)

$Tl(CF_3)_3 \cdot 2dmso$. Raman: 206 vs, 227 s, 317 w, 336 w, 410 w, 518 w, 686 s, 708 s, 719 m, 959 w, 1004 w, 1067 vw, 1100 w, 1122 vw, 1145 m, 1422 w, 1425 w, 1438 vw, 2940 m, 3023 m. IR (CsBr): 215 vs, 225 vs, 310 m, 339 s, 402 vs, 513 vw, 680 vw, 708 s, 715 s, 911 w, 952 vs, 1003 vs, 1020–1200 vs,br, 1218 vw, 1306 vw, 1323 vw, 1359 vw, 1389 vw, 1415 w, 1422 m, 1445 w, 1662 w, 1906 vw, 1950 vw, 1980 vw, 2218 vw, 2250 vw, 2937 w, 3022 w.

$Tl(CF_3)_3 \cdot 2py$. Raman: 209 vs, 226 m, 423 vw, 522 w, 631 vw, 663 w, 717 m, 1018 s, 1048 s, 1080 w, 1102 vw, 1118 vw, 1134 vw, 1147 w, 1169 vw, 1588 w, 1612 w, 3097 m. IR (CsBr): 217 s, 225 s, 417 w, 511 vw, 515 vw, 611 s, 702 vs, 757 vs, 887 vw, 949 vw, 1034 vs, 1052 vs, 1095 vs, 1125 vs, 1139 s, 1157 s, 1222 w, 1229 w, 1237 vw, 1254 vw, 1367 vw, 1391 vw, 1450 m, 1492 vw, 1526 vw, 1602 m, 1624 vw, 1633 vw, 1664 vw, 1813 vw, 1889 vw, 1930 vw, 2018 vw, 2467 vw, 2968 vw, 3089 vw.

Mass spectra of the $Tl(CF_3)_3$-complexes (only ^{205}Tl containing fragments)

$Tl(CF_3)_3 \cdot 2dmf$ (70 eV, 20 °C, *m/e*): 416 ($[Tl(CF_3)_2 \cdot dmf]^+$, 14.1%); 343 ($Tl(CF_3)_2^+$, 16.0%); 278 ($[Tl \cdot dmf]^+$, 56.1%); 274 ($Tl(CF_3)^+$, 30.5%); 224 (TlF^+, 1.6%); 205 (Tl^+, 100%). Other low intensity ions have been omitted. Ions with *m/e* values between 73 and 42 can be assigned to fragmentation products of dmf, $[CF_3]^+$, and $[CF_2]^+$.

$Tl(CF_3)_3 \cdot 2dmso$ (70 eV, 20 °C, *m/e*): 567 ($[Tl(CF_3)_3 \cdot 2dmso]^+$, 0.1%); 421 ($[Tl(CF_3)_2 \cdot dmso]^+$, 5.6%); 343 ($Tl(CF_3)_2^+$, 2.1%); 283 ($[Tl \cdot dmso]^+$, 16.4%); 274 ($Tl(CF_3)^+$, 5.4%); 224 ($TlF^+$, 0.2%); 205 ($Tl^+$, 47.9%). Further peaks between 78 and 44 can be assigned to fragments from dmso, $[CF_3]^+$, and $[CF_2]^+$.

$Tl(CF_3)_3 \cdot 2py$ (70 eV, 20 °C, *m/e*): 422 ($[Tl(CF_3)_2 \cdot py]^+$, 7.2%); 343 ($Tl(CF_3)_2^+$, 3.7%); 284 ($[Tl \cdot py]^+$, 14.6%); 274 ($Tl(CF_3)^+$, 7.2%); 224 (TlF^+, 0.5%); 205 (Tl^+, 66.8%). Further peaks between 79 and 39 can be assigned to pyridine fragments, $[CF_3]^+$, and $[CF_2]^+$.

Table 9

^{19}F-chemical shifts for $Ga(CF_3)$-derivatives after various reaction times (δ (ppm))

	CH_3CN/glyme		CH_3CN/diglyme		dmf
	2d	7d	7d	11d	4d
$Ga(CF_3)_3 \cdot D$	−54.60	−54.60	−51.84	−52.31	−50.95
$Ga(CF_3)_2Cl \cdot D$	−57.07	−56.99	−53.10	−53.62	−53.72
$Ga(CF_3)Cl_2 \cdot D$	−59.10	–	−54.60	–	−56.14

Table 10

^{19}F NMR spectrum of the reaction mixture in dmso (Fig. 3)

δ (ppm)	Assignment
−42.99	In(CF_3)-compound [a]
−43.22	In(CF_3)-compound
−44.16	In(CF_3)-compound
−44.76	S$(CF_3)_2$ [b]
−45.17	In(CF_3)-compound
−46.46	In(CF_3)-compound
−73.17	SO$(CF_3)_2$ or $SO_2(CF_3)_2$ [c]

[a] Compounds of the general formula: $In(CF_3)_{3-x-y}(CH_3)_xCl_y$ ($x + y \leq 3$, $x = 0$–2; $y = 0$–2). [b] $S(CF_3)_2$: δ −38.64 ppm [31], δ −45.50 ppm, $^1J(^{19}F-^{13}C)$ 313.7 Hz (CH_2Cl_2) (self-measured sample of authentic material). [c] $SO(CF_3)_2$: δ −70 ppm [32], δ −64.5 ppm [33]; $SO_2(CF_3)_2$: δ −74 ppm [34].

The reaction of $Cd(CF_3)_2 \cdot 2CH_3CN$ with $InCl_3$ in dmso

Whereas the reactions in CH_3CN, dmf, and pyridine proceeded selectively to form $In(CF_3)_{3-x}Cl_x \cdot D$ and $Cd(CF_3)Cl \cdot D$, two by-products were detected in dmso solution. Complexation of $Cd(CF_3)_2 \cdot 2CH_3CN$ was observed before it reacted with the indium halide. The change in the absolute value of the coupling constant $^2J(^{111/113}Cd-^{19}F)$ indicates that the acetonitrile molecules are replaced by dmso ($Cd(CF_3)_2 \cdot 2$dmso: $^2J(^{111/113}Cd-^{19}F)$ 369/383 Hz [23], $Cd(CF_3)_2 \cdot 2CH_3CN$: $^2J(^{111/113}Cd-^{19}F)$ 446/466 Hz [26]). ^{19}F NMR data are given in Table 10.

Preparation of $Tl(CF_3)_3 \cdot 2$dmso

To a solution of $Tl(CF_3)_3 \cdot 2$dmf in dmf at 40 °C was added an excess of dmso. The solvent was distilled off in vacuo at ca. 40 °C, and the residue was purified by a repeated recrystallisation from CH_3CN. Further crystallisation from diethyl ether gave colourless crystals of $Tl(CF_3)_3 \cdot 2$dmso in approximately 30% yield (m.p. 104 °C). Analytical data are summarized in Tables 11 and 12.

Preparation of $Tl(CF_3)_3 \cdot 2$py

A solution of $Tl(CF_3)_3 \cdot 2$dmf in a ten-fold molar excess of pyridine contained in a Schlenk-tube was warmed to 50–60 °C. Pyridine was distilled off from the yellow solution. Repetition of the procedure with warming to 90–100 °C yielded a crude

Table 11

^{19}F and ^{1}H NMR spectroscopic data for $Tl(CF_3)_3$-complexes

	^{19}F δ (CF_3) (ppm)	$^2J(^{203/205}Tl-^{19}F)$ (Hz)	^{1}H δ (solvent) (ppm)
$Tl(CF_3)_3 \cdot 2$dmf [a]	−36.8	3010/3040	2.83/2.96/8.89
dmf (neat) [b]			2.81/2.98/7.89
$Tl(CF_3)_3 \cdot 2$dmso	−36.05 [c]	2978/3006	2.67
dmso (neat) [b]			2.62
$Tl(CF_3)_3 \cdot 2$py	−35.16	2940/2970	7.44/7.87/8.50
py (neat) [d]			7.14/7.55/8.51

[a] In CD_3CN. [b] Ref. 35. [c] $^1J(^{19}F-^{13}C)$ 380.5 Hz, $^4J(^{19}F-^{19}F)$ 4.1 Hz, $^1\Delta(^{19}F-^{12/13}C)$ 0.1405 ppm. [d] Ref. 36.

Table 12

Elemental analysis and results of molecular weight determinations for the $Tl(CF_3)$-complexes

Compound	Elemental analysis (Found (calc.) (%))			Molecular weight (in dmso)
	C	H	N	Found (calc.) (%)
$Tl(CF_3)_3 \cdot 2dmf$	19.6	2.6	5.2	557
	(19.4)	(2.5)	(5.0)	(558)
$Tl(CF_3)_3 \cdot 2dmso$	15.3	2.1	-	557
	(14.1)	(2.1)	(-)	(568)
$Tl(CF_3)_3 \cdot 2py$	28.2	1.9	4.8	
	(27.4)	(1.8)	(4.9)	

product with excellent solubility in diethyl ether. Crystallisation at −40 °C gave white crystals decomposing at 86 °C. The solid still contained 3% of $Tl(CF_3)_3 \cdot 2dmf$. Analytical data are summarized in Tables 11 and 12.

Reactions with thallium triacetate and tris(trifluoroacetate)

The thallium acetates were dissolved in CH_2Cl_2, dmf, or pyridine at room temperature. At the beginning only half of the required $Cd(CF_3)_2 \cdot$ diglyme was added, but after the mixtures had been stirred for 24 hours (3 hours in pyridine) the remainder of the cadmium complex was introduced. The stoichiometry was about 1 : 3 ($Tl(OCOR)_3 : Cd(CF_3)_2 \cdot$ diglyme). The species $[Tl(CF_3)_4]^-$ was shown by ^{19}F NMR spectroscopy to be the main product: ($[Tl(CF_3)_4]^-$: δ (CF_3) -33.4 ppm, $^2J(^{205}Tl-^{19}F)$ 2080 Hz (in CH_2Cl_2); δ (CF_3) $- 33.8$ ppm, $^2J(^{205}Tl-^{19}F)$ 2100 Hz (in dmf)). CH_3COF was formed as a by-product in the reaction with $Tl(OCOCH_3)_3$ in CH_2Cl_2.

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