absorption band in $[Ta_6Cl_{12}](OMe)_2 \cdot 4MeOH$. The same is observed for the strong doublet in the region of 400 cm^{-1} originating from Ta–O stretching (from OCH_3 groups). These shifts should be the consequence of the shortening of the Ta–OMe terminal bond distances in the compounds containing the $[Ta_6Cl_{12}]^{4+}$ unit as compared to those compounds of the $[Ta_6Cl_{12}]^{2+}$ unit. This effect was previously observed and confirmed by the crystal structure determination for $[Nb_6Cl_{12}]^{n+}$ and $[Ta_6Cl_{12}]^{n+}$ (n = 2–4) analogues.[15,24] The deuteriated form of $Na_2[Ta_6Cl_{12}](OMe)_6$ shows significant shifts of all CD_3 vibrations to lower wavenumbers, as expected.[25]

^{1}H NMR Spectra. Proton magnetic resonance spectra of all $M'_2[Ta_6Cl_{12}](OMe)_6 \cdot 6MeOH$ were recorded in highly concentrated methanol-d_4 solutions. The spectrum of the lithium compound is shown in Figure 2. Between the methyl proton signal of the methanol at 3.30 ppm and hydroxyl proton signal at 5.09 ppm there is a sharp peak at 4.21 ppm, indicating the presence of protons of the methoxide ligands. The sharpness of this peak indicates the equivalency among the six methoxide ligands present. Slow exchange of the methoxide ligands with solvent methanol leads to a decrease in intensity of the signal at 4.21 ppm, which becomes noticeable after 1 h.

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Preparation of Bis(trifluoromethyl)tellurium, Bis(trifluoromethyl)selenium, Bis(trifluoromethyl)diselenium, Tris(trifluoromethyl)antimony, Tris(trifluoromethyl)arsine, Bis(trifluoromethyl)arsenic Iodide, Tris(trifluoromethyl)phosphine, and (Trifluoromethyl)phosphorus Diiodide by Reaction of Bis(trifluoromethyl)mercury with the Group 5 and 6A (15 and 16) Halides

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The reactions between $Hg(CF_3)_2$ and representative halides of the lower elements of main groups 5 (15) and 6A (16) have been investigated. At 155 °C the reaction between $TeBr_4$ and $Hg(CF_3)_2$ affords $Te(CF_3)_2$ in 92% yield. In 4.5 h at 210 °C $SeBr_4$ and $Hg(CF_3)_2$ form $Se(CF_3)_2$ and $Se_2(CF_3)_2$ in 67% and 3% yields, respectively; in 2.5 h at 170 °C they generate $Se(CF_3)_2$ and $Se_2(CF_3)_2$ in 26% and 57% yields, respectively. At 165 °C SbI_3 and $Hg(CF_3)_2$ produce $Sb(CF_3)_3$, 63%. The interaction of AsI_3 and $Hg(CF_3)_2$ can result in either $As(CF_3)_3$, 75%, or $As(CF_3)_2I$, 54%. Similarly, exposure of PI_3 to $Hg(CF_3)_2$ can synthesize either $P(CF_3)_3$, 55%, or $P(CF_3)I_2$, 37%. In general, these reactions are more convenient than the classic route pioneered by Emeleus and his students, the interactions of trifluoromethyl iodide with the elements.

Introduction

Perfluoroalkyl derivatives of the late main-group elements, the elements of groups 5A (15) and 6A (16), are currently under examination for a variety of reasons. The central thrust of various studies ranges from detailing the differences in reactivity afforded by the "substitution" of more electronegative perfluoroalkyl groups for perhydroalkyl substitutents in ligands like thiolates, alkoxides, and phosphides, e.g., $Mo(CO)_3(Cp)SCF_3$,[1] Re(C-*t*-Bu)(NAr)-$(OCMe(CF_3)_2)_2$,[2] and $Fe(CO)_2(Cp)P(CF_3)_2$,[3] to studying multiply bonded compounds of the heavier atoms, e.g., $CF_3P{=}CF_2$[4] and $CF_3As{=}CF_2$,[5] to assessing high-valent oxo acids as fuel cell electrolytes, e.g., $(CF_3)_2P(O)OH$.[6] Potential uses of perfluoroalkyl-substituted ligands include the fine tuning of the electronic properties of a metal complex by means of a judicious selection of the groups attached to, for example, a phosphine, thereby enhancing the catalytic properties of the system,[7] or the introduction of chiral centers by ligands such as $PMe(Ph)(CF_3)$.

Although a variety of alternative syntheses of the trifluoromethyl derivatives of the lower group 5 and 6A elements have been proposed, in practice the procedure almost universally employed is based upon that originally developed by Emeleus and his students during the period 1949–1958. These preparations involve the reactions of any of the elements P, As, Sb, S, and Se with CF_3I at elevated temperatures, 165–285 °C, and high pressures, ca. 50 atm.[8-12] While this type of reaction has been

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repeatedly utilized to successfully generate desired trifluoromethyl derivatives of the elements detailed above, there are several drawbacks inherent to the method. Among the less desirable features of some of the various protocols are the uses of steel autoclaves, which often must be passivated by sacrificing the first run of the preparation, molten salt baths for relatively precise temperature control, expensive reagents, extensive recycling, and product separations, which may be lengthy.

Previously we have examined the ligand-exchange reactions between the mercurial $Hg(CF_3)_2$ and a variety of different types of metal halides.[13-15] Although there are exceptions, for relatively electron-poor elements the thermal stability of the anticipated trifluoromethylated product is usually insufficient to withstand the temperatures required for the exchange between the mercurial and the metal halide to proceed at reasonable rates.[14] The trifluoromethyl derivatives of the relatively electron-rich group 5 and 6A elements, however, are among the most stable known. Thermal decomposition is not observed even at temperatures far in excess of the 100–130 °C that has been previously employed in successful ligand-exchange reactions utilizing $Hg(CF_3)_2$.[16,17]

The overall objective of this study was to determine whether ligand-exchange reactions between $Hg(CF_3)_2$ and representative halides of the elements Te, Se, Sb, As, and P would occur to generate the trifluoromethyl derivatives of these elements in reasonable yield or if the presence of the (Lewis) acidic mercurial salts in the reaction mixtures might catalyze the decomposition of the $M-CF_3$ linkage (forming the metal fluoride), as has been previously observed, for example, in the more fully substituted (trifluoromethyl)germanes and -stannanes.[16,17] An additional objective of this study was to examine the possibility of controlling the composition of the product mixture obtained by altering either the thermal conditions or the exposure times in order to enhance the amounts of partially substituted derivatives, compounds like $As(CF_3)_2I$ or $P(CF_3)I_2$, that were isolated.

Since high-yield alternative syntheses of both $S(CF_3)_2$ and $S_2(CF_3)_2$ currently exist,[18,19] the formation of these compounds by reactions with $Hg(CF_3)_2$ was not studied at this time. Examination of the bismuth trihalides was also deferred since $Bi(CF_3)_3$ is known to decompose at 100 °C.[20]

Experimental Section

General Procedures. Compound manipulations were carried out in glovebags, in gloveboxes, or with standard vacuum lines. Mass spectral data at 70 eV were recorded on an AEI MS-30 (double focussing) or on a Hewlett-Packard 5985A (quadrupole) instrument. The former operated with the source at ambient temperature, and the latter with the source at 200 °C. Volatile samples were introduced through a gas-phase inlet system (MS-30) or by injection onto a GC–MS column (HP 5985A); less volatile solids were examined by means of solid probe techniques. Ambient temperature ^{19}F, ^{31}P, ^{13}C, ^{125}Te, and ^{77}Se NMR spectra were obtained from neat samples contained in sealed 4-mm tubes with IBM 200-SY or Bruker AM-400 spectrometers; external D_2O was employed as the lock solvent. Positive chemical shifts are deshielded relative to the standards, external CF_3CO_2H, 85% H_3PO_4, $Si(CH_3)_4$, $Te(CH_3)_2$, and $Se(CH_3)_2$, respectively.

Bis(trifluoromethyl)mercury, formed from the thermal decarboxylation of $Hg(CF_3CO_2)_2$,[13] was twice sublimed prior to use. Phosphorus triiodide and SbI_3 were prepared by interaction of the elements with I_2 in CH_2Cl_2 or C_6H_6; AsI_3 was generated from the oxide by reaction with KI in concentrated HCl.[21] The triiodides were purified by sublimation at 30, 110, or 150 °C. Purity confirmation was by melting point determination. Tellurium tetrabromide and $SeBr_4$ were purchased from Strem Chemicals and used as obtained.

Table I. Chemical Shifts (ppm) and Couplings (Hz) for Group 5 and 6A Trifluoromethyl Compounds

group 5A (15)	$\delta(^{19}F)$	$\delta(^{13}C)$	$^1J_{C-F}$	group 6A (16)	$\delta(^{19}F)$	$\delta(^{13}C)$	$^1J_{C-F}$
$Sb(CF_3)_3$	35.4	132.8	359	$Te(CF_3)_2$	54.5[d]	105.9	352
$As(CF_3)_3$	28.6	128.3	340	$Se(CF_3)_2$	43.1[e]	122.5	331
$As(CF_3)_2I$	23.9			$Se_2(CF_3)_2$	37.1[f]	118.4	336
$As(CF_3)I_2$	18.9						
$P(CF_3)_3$	24.1[a]	126.6	316				
$P(CF_3)_2I$	18.8[b]						
$P(CF_3)I_2$	14.2[c]						

[a] $\delta(^{31}P) = -1.7$ ppm; $^2J_{P-F} = 85$ Hz. [b] $\delta(^{31}P) = 0.8$ ppm; $^2J_{P-F} = 70$ Hz. [c] $\delta(^{31}P) = 57.1$ ppm; $^2J_{P-F} = 48$ Hz. [d] $\delta(^{125}Te) = 1368$ ppm; $^2J_{Te-F} = 32$ Hz. [e] $\delta(^{77}Se) = 718$ ppm. [f] $\delta(^{77}Se) = 548$ ppm.

Reactions of Main Group 6 Halides with $Hg(CF_3)_2$. Formation of $Te(CF_3)_2$. Under inert atmosphere, $TeBr_4$, 1.1493 g (2.57 mmol), and $Hg(CF_3)_2$, 2.6087 g (7.70 mmol), were placed into a cylindrical reactor fashioned from 20-mm Pyrex tubing. The reactor, 80 mm in length, was cooled to −196 °C, evacuated through an attached 4-mm Teflon valve, and then heated to 155 ± 5 °C in an oil bath containing silicone oil. After 2.5 h, the reaction was terminated and the volatile contents of the reactor were removed to a vacuum line and then fractionated. Most of the material (ca. 92%) passing through the −131 °C trap (0.4444 g) was CF_3Br. The product, bright yellow $Te(CF_3)_2$, 0.6268 g (2.36 mmol), passed through a trap held at −95 °C but was retained at −116 °C. The isolated yield was 92%. Confirming NMR data are contained in Table I. Mass spectrometry of the residual solid demonstrated the presence of $Hg(CF_3)_2$, $Hg(CF_3)Br$, and $HgBr_2$.

Formation of $Se(CF_3)_2$. Selenium tetrabromide, 0.8387 g (2.10 mmol), and $Hg(CF_3)_2$, 2.1328 g (6.30 mmol), were similarly loaded into a reactor and then heated to 170 ± 5 °C for 25 h. The reactor was cooled to −10 °C, and the products volatile at that temperature were fractionated on the vacuum line. Fluorocarbons were removed by passage through a −131 °C bath. The mixture retained in the −131 °C bath was fractionated at −116 °C. The material passing through this bath was clear, colorless $Se(CF_3)_2$. The yield of $Se(CF_3)_2$, 0.2054 g (0.947 mmol), was 45%, based upon the amount of $SeBr_4$ taken. The material held in the −116 °C bath was yellow $Se_2(CF_3)_2$, 0.0385 g (0.13 mmol), which formed in 12% yield. Confirming NMR data are in Table I.

In a separate reaction $SeBr_4$, 0.6927 g (1.74 mmol), and $Hg(CF_3)_2$, 1.7675 g (5.22 mmol), were held at 180 °C for 12 h. Separation as above gave $Se(CF_3)_2$, 0.1251 g (0.577 mmol), 33%, and $Se_2(CF_3)_2$, 0.1095 g (0.370 mmol), 43%.

After 2.5 h at 170 °C, $SeBr_4$, 0.6588 g (1.65 mmol), and $Hg(CF_3)_2$, 1.6853 g (4.98 mmol), gave $Se(CF_3)_2$, 0.0937 g (0.432 mmol), 26%, and $Se_2(CF_3)_2$, 0.1381 g (0.467 mmol), 57%.

In a fourth reaction $SeBr_4$, 0.7441 g (1.865 mmol), and $Hg(CF_3)_2$, 1.9198 g (5.670 mmol), were held at 210 °C for 4.5 h. Separation as above resulted in $Se(CF_3)_2$, 0.2706 g (1.247 mmol), 67%, and $Se_2(CF_3)_2$, 0.0087 g (0.029 mmol), 3%.

Reactions of Main Group 5 Iodides with $Hg(CF_3)_2$. Formation of $Sb(CF_3)_3$. Antimony triiodide, 1.6752 g (3.33 mmol), and $Hg(CF_3)_2$, 3.9866 g (11.77 mmol), were analogously introduced into a reactor, and the reagents were heated to 165 ± 5 °C. After every 2 h the reactor was cooled to −10 °C and the volatile contents were removed and fractionated at −63 °C. The material retained at that temperature was returned to the reactor and again heated to 165 °C; the material passing through the −63 °C bath was set aside until the end of the reaction. Although the vast majority of the stibines were produced during the first 2 h, the reaction was continued until no further $Sb(CF_3)_3$ was recovered, 8 h.

Separation at −131 °C yielded CF_3I. Although traces of $(CF_3)_2SbI$, ca. 2%, were also recovered, tris(trifluoromethyl)stibine was the major product. The colorless species, $Sb(CF_3)_3$, 0.6899 g (2.098 mmol), was isolated in 63% yield based upon the amount of SbI_3 employed.

In a separate reaction SbI_3, 0.8958 g (1.78 mmol), and $Hg(CF_3)_2$, 0.8880 g (2.62 mmol), were allowed to interact for a total of 1 h at 190 °C. The reactor was cooled to −10 °C, and all of the material that was volatile at that temperature was removed. Separation resulted in $Sb(CF_3)_3$, 0.1405 g (0.43 mmol), 25%, based upon SbI_3. See Table I.

Formation of $As(CF_3)_3$. Arsenic triiodide, 2.243 g (4.92 mmol), and $Hg(CF_3)_2$, 2.500 g (7.38 mmol), were separately placed into a reactor of the type described above, the dinitrogen was removed, and the vessel contents were heated to 165 °C for 2 h. The reactor was cooled to −10 °C, and the volatile contents were removed and fractionated at −78 °C.

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Table II. Trifluoromethylation Reactions of Main Group 5 and 6 Halides with $Hg(CF_3)_2$

reactants	major products	conditions: *t*, h; *T*, °C	% yield $Hg(CF_3)_2 + MX_n$	% yield $CF_3I + M$[a]
		Group 6		
$Hg(CF_3)_2 + TeBr_4$	$Te(CF_3)_2$	2.5; 155	92	0[b]
$Hg(CF_3)_2 + SeBr_4$	$Se(CF_3)_2 + Se_2(CF_3)_2$	4.5; 210	67; 3	48;13[c]
$Hg(CF_3)_2 + SeBr_4$	$Se(CF_3)_2 + Se_2(CF_3)_2$	25; 170	45;12	
$Hg(CF_3)_2 + SeBr_4$	$Se(CF_3)_2 + Se_2(CF_3)_2$	12; 180	33; 43	
$Hg(CF_3)_2 + SeBr_4$	$Se(CF_3)_2 + Se_2(CF_3)_2$	2.5; 170	26; 57	
		Group 5		
$Hg(CF_3)_2 + SbI_3$	$Sb(CF_3)_3$	8; 165	63	64
$Hg(CF_3)_2 + SbI_3$	$Sb(CF_3)_3$	1; 190	25	
$Hg(CF_3)_2 + AsI_3$	$As(CF_3)_3$	34; 165	75	70
$Hg(CF_3)_2 + AsI_3$	$As(CF_3)_3$	2; 210	63	
$Hg(CF_3)_2 + AsI_3$	$As(CF_3)_2I + As(CF_3)_3$	137; 160	54; 16	
$Hg(CF_3)_2 + PI_3$	$P(CF_3)_3$	68; 160	55	35
$Hg(CF_3)_2 + PI_3$	$P(CF_3)_3$	2; 210	41	
$Hg(CF_3)_2 + PI_3$	$P(CF_3)I_2 + P(CF_3)_2I$	12; 140	37; 8	

[a] Where possible, yield data for these reactions have been converted from those reported (yield based upon amount of CF_3I consumed)[8-10,12] to yield based upon the amount of limiting reagent. [b] The formation of $Te(CF_3)_2$ from the interaction of CF_3I with Te has not been reported. [c] In a flow reactor with a contact time of 120 s, Se and CF_3I are reported to yield $Se(CF_3)_2$, 15%, and $Se_2(CF_3)_2$, 65%.[28]

The retained liquid was returned to the reactor, which was again heated to 165 °C. The procedure was repeated every 2 h for 34 h.

All of the recovered volatile material was separated by fractionation at −95 and −131 °C into $As(CF_3)_3$, 1.041 g (3.69 mmol), 75%, based upon AsI_3, and CF_3I. Very small amounts of $As(CF_3)_2I$ and $As(CF_3)I_2$ were also observed (see below).

Alternatively, AsI_3, 1.5021 g (3.29 mmol), and $Hg(CF_3)_2$, 1.6793 g (4.96 mmol), were held at 210 °C for 2 h. Tris(trifluoromethyl)arsine, 0.5808 g (2.06 mmol), was then isolated in 63% yield (see Table I).

Formation of $As(CF_3)_2I$. Arsenic triiodide, 0.400 g (0.877 mmol), was combined with $Hg(CF_3)_2$, 0.457 g (1.35 mmol), in a 12 × 200 mm reactor, and after evacuation, the vessel was heated to 160 °C for a total of 20 h. After every 2 h, all of the material that was volatile at −10 °C was removed from the reactor. The remaining contents of the vessel were then heated to 160 °C for 117 h, after which all of the volatile products were removed and combined with those previously obtained.

Separation by fractionation yielded bright yellow $As(CF_3)I_2$, 0.021 g (0.05 mmol), 6%, which was held in a −30 °C trap, colorless $As(CF_3)_3$, 0.040 g (0.14 mmol), 16%, which was retained in a −131 °C trap, and CF_3I, 0.121 g (0.62 mmol), 23%. The major component of the mixture, however, was $As(CF_3)_2I$, 0.161 g (0.47 mmol), 54% based upon AsI_3. See Table I.

Formation of $P(CF_3)_3$. Under N_2, a reactor was loaded with PI_3, 2.002 g (4.86 mmol), and $Hg(CF_3)_2$, 2.470 g (7.29 mmol), the noncondensable gases were evacuated, and the reagents were heated to 160 °C for 68 h. At the termination of the reaction, the vessel was cooled to −10 °C and the volatile contents were removed to the vacuum line through a −78 °C bath. The material passing through the −78 °C trap was fractionated at −131 °C to remove CF_3I and PF_3 and then at −95 °C. The amount of $P(CF_3)_3$ that passed through the −95 °C trap, 0.636 g (2.67 mmol), corresponded to a 55% yield (see Table I).

Similarly, PI_3, 0.9424 g (2.29 mmol), and $Hg(CF_3)_2$, 1.1668 g (3.45 mmol), were heated at 210 °C for 2 h. Fractionation yielded $P(CF_3)_3$, 0.2215 g (0.931 mmol), 41%.

Formation of $P(CF_3)I_2$. Excess PI_3, 0.354 g (0.859 mmol), and $Hg(CF_3)_2$, 0.167 g (0.49 mmol), were placed into a reactor that was attached to a vacuum line, evacuated while at −196 °C, and then heated to 140 °C. Every 2 h, the contents of the vessel were cooled to −10 °C and all products volatile at that temperature were removed, whereupon heating was resumed for another 2 h. After a total of 12 h the reaction ceased.

The dark red liquid recovered was separated, and the material that passed through a −10 °C bath but was held at −30 °C was identified as $P(CF_3)I_2$ (see Tables I and II). Based upon the moles of $Hg(CF_3)_2$ originally taken, the isolated yield of $P(CF_3)I_2$, 0.063 g, 0.18 mmol), corresponded to 37%. Small amounts of $P(CF_3)_2I$, 8%, were also isolated.

Results and Discussion

The isolated yields of the various trifluoromethylated derivatives that were prepared during the course of this study and the conditions under which they were formed have been collected in Table II. For comparison, the yields of the compounds obtained from the interaction of CF_3I with the elements at elevated temperatures are also presented in Table II (see, however, footnotes *a–c*). The most dramatic difference between the results of the two methods is that $Te(CF_3)_2$, which has not as yet been isolated from reactions between CF_3I and the element, is easily prepared in 92% yield from the reactions between the mercurial $Hg(CF_3)_2$ and $TeBr_4$. Generally, the yields of the other products reported here are somewhat greater than those obtained from the reactions of CF_3I with the elements (see Table II).

Collectively, all of these syntheses represent very convenient preparations of the trifluoromethylated compounds considered. Although we are aware of no reason that the reactions could not have been carried out in autoclaves, all of these experiments utilized vessels constructed from standard wall Pyrex tubing to which 4-mm Teflon valves had been fused. Aside from the desired trifluoromethylated derivatives, the major volatile products consisted of the appropriate trifluoromethyl halide, CF_3I or CF_3Br, and, for the group 5A (15) compounds, the trifluoromethylated derivatives containing fewer or, for $P(CF_3)I_2$ and $As(CF_3)_2I$, more CF_3 groups. Minor components, which were not always observed, included small amounts of SiF_4, traces of C_2F_4 and C_3F_6, and, for the group 6A (16) compounds, CF_2Br_2. Trifluorophosphine and AsF_3 were formed in small amounts in the PI_3 and AsI_3 reactions, respectively. Separation procedures involving fractional condensations with conventional slush baths proved adequate for purification.

All of the reactions are somewhat temperature sensitive, as is shown in Table II for $SeBr_4$, SbI_3, AsI_3, and PI_3. With the exception of $Se(CF_3)_2$, which is further discussed below, the highest yields are obtained with less elevated temperatures but much longer reaction times. For AsI_3 and PI_3, the decrease in the isolated yields of the trisubstituted compounds is only about 10–15% even if the reaction temperature is increased by ca. 50 °C. This is not the case for the SbI_3 reaction, however, since the product, $Sb(CF_3)_3$, begins to decompose near 180 °C. For the antimony reaction, reasonably precise temperature control is required.

Both the mass and the NMR spectra, the latter found in Table I, are in complete accord with the formulation of the compounds as expressed and, where available, with that found in the literature.[13,22-27] As shown in Table I, the expected trends within this

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data set are evident. For example, other things being equal, ascending the periodic table results in a shielding of the ^{19}F resonance of ca. 4–5 ppm from $As(CF_3)_3$ to $P(CF_3)_3$ or from $As(CF_3)I_2$ to $P(CF_3)I_2$ and slightly more from $Sb(CF_3)_3$ to $As(CF_3)_3$. Similarly, in the group 6A derivatives, i.e., from $Te(CF_3)_2$ to $Se(CF_3)_2$, the ^{19}F resonance is shielded, here by 11 ppm. The ^{13}C–F coupling constants decrease as the size of the central atom decreases. The mass spectra, which will be discussed separately, were as expected; they contain all of the ions anticipated for each compound including the appropriate molecular ion, the $(M - F)^+$ ion, and the $(M - CF_3)^+$ ion in each case. Ions of mass greater than the molecular ion were not observed.

For the group 5A elements one of the principal differences between the reactions of antimony and the others that were examined here is related to the observation that the activation energy for self-exchange (redistribution) reactions decreases as the group is descended.[10] Thus, in addition to ligand interchanges between the antimony and the mercury centers like those depicted in eq 1 and 2, redistribution reactions between antimony centers, like that shown in eq 3, contribute significantly. Under the conditions employed here, this last reaction controls the product distribution.

$$Hg(CF_3)_2 + SbI_3 \rightarrow Hg(CF_3)I + Sb(CF_3)I_2 \qquad (1)$$

$$Hg(CF_3)_2 + Sb(CF_3)I_2 \rightarrow Hg(CF_3)I + Sb(CF_3)_2I \qquad (2)$$

$$2Sb(CF_3)_2I \rightarrow Sb(CF_3)_3 + Sb(CF_3)I_2 \qquad (3)$$

The analogous redistribution reactions of phosphorus and arsenic are also well-known, but typically they occur much more slowly than the antimony reactions.[10] This is the principal reason that arsenic and phosphorus derivatives which are only partially trifluoromethylated, e.g., $As(CF_3)_2I$ and $P(CF_3)I_2$, can be intercepted by periodically cooling the reactor to −10 °C (which retains the volatile $Hg(CF_3)_2$ within the vessel) and then removing the incompletely substituted species whereas, as yet, we have been unable to separate reasonable amounts of the partially substituted trifluoromethyl derivatives of antimony by a similar procedure.

In part, the higher yield of the group 6A (16) compound $Te(CF_3)_2$, relative to the yield of $Se(CF_3)_2$, appears to be a reflection of the lesser stability of the Te–Te bond relative to that of the Se–Se bond. During the early stages of the $Te(CF_3)_2$ syntheses, the reactor contents assume a very deep red coloration similar to that associated with $Te_2(CF_3)_2$,[13] but within a few minutes this hue fades, and then only the straw-yellow color of $Te(CF_3)_2$ is observed. However, by a judicious selection of the reaction conditions, substantial amounts of the monovalent $Se_2(CF_3)_2$, 57%, can be obtained. As shown in Table II, the isolated amounts of the diselenide decrease substantially with longer reaction times or higher temperatures.

For both $TeBr_4$ and $SeBr_4$, redox reactions clearly occur at a very early stage of the transformation. Overall, this early stage can be represented as shown in eq 4. This first stage of the reaction consists of (at least) a two-step process, and whether the first step is the reduction of $SeBr_4$ by the elimination of bromine, which then rapidly cleaves the mercury–carbon bond in $Hg(CF_3)_2$, forming $Hg(CF_3)Br$ and CF_3Br, or whether the first step is the formation of $Se(CF_3)Br_3$ by ligand exchange, the product quickly eliminating CF_3Br, is currently unproven, although the latter is currently thought to be the case. Reductive sequences, similar in principle to that shown in eq 4, would generate monovalent group 6A (16) derivatives, as shown in eq 5a and 5b.

$$SeBr_4 + Hg(CF_3)_2 \rightarrow SeBr_2 + Hg(CF_3)Br + CF_3Br \qquad (4)$$

$$2SeBr_2 + Hg(CF_3)_2 \rightarrow Se_2Br_2 + Hg(CF_3)Br + CF_3Br \qquad (5a)$$

$$2Se(CF_3)Br + Hg(CF_3)_2 \rightarrow Se_2(CF_3)_2 + Hg(CF_3)Br + CF_3Br \qquad (5b)$$

The fact that CF_3I is isolated from the reactions of the main group 5 iodides with $Hg(CF_3)_2$ indicates that reduction of these elements also occurs to some extent. Whether this is a side reaction or whether the reaction pathway to the trifluoromethylated products consists primarily of reduction followed by reoxidation of the group 5A center is currently under examination.

Aside from the present study, there have been only two reports of the formation of trifluoromethyl-substituted derivatives of the elements of either group 5A (15) or group 6A (16) using mercurials. Both involved the synthesis of trifluoromethyl group 6A species. In the first, the reaction of elemental selenium with $Hg(CO_2CF_3)_2$ yielded $Se_2(CF_3)_2$ in 16% yield.[29] During the second study, an attempt to generate $Te(CF_3)_2$ using $Hg(CO_2CF_3)_2$ and $TeCl_4$, the vessel exploded.[30] In this second report the interaction of $TeCl_4$ with $Hg(CF_3)_2$ was stated to form $Te(CF_3)_2$ in ca. 56% yield, but somewhat curiously, an examination of the reaction between $TeBr_4$ and $Hg(CF_3)_2$ was claimed to be unproductive.[30] In actuality, as demonstrated above, the interaction of $TeBr_4$ with $Hg(CF_3)_2$ generates $Te(CF_3)_2$ in 92% yield; the separation is trivial.

In summary, the reactions of $Hg(CF_3)_2$ with the representative halides of main groups 5 and 6 examined here provide very convenient syntheses of the trifluoromethylated derivatives of these elements. The advantages over previous methods include ease of handling of the reagents, all solids, less difficulty in the separation steps, and the convenience of employing standard oil baths and glassware during the reactions. An added advantage is that CF_3CO_2H, the source of the CF_3 group here, is much less expensive than CF_3I, the most common alternative source of the CF_3 functionality.[31]

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Registry No. $Hg(CF_3)_2$, 371-76-6; $TeBr_4$, 10031-27-3; $Te(CF_3)_2$, 55642-42-7; $SeBr_4$, 7789-65-3; $Se(CF_3)_2$, 371-79-9; $Se_2(CF_3)_2$, 372-65-6; SbI_3, 7790-44-5; $Sb(CF_3)_3$, 432-05-3; AsI_3, 7784-45-4; $As(CF_3)_3$, 432-02-0; $As(CF_3)_2I$, 359-55-7; PI_3, 13455-01-1; $P(CF_3)_3$, 432-04-2; $P(CF_3)I_2$, 421-59-0; $P(CF_3)_2I$, 359-64-8.

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(31) Recent prices (1988) from one typical supplier (Aldrich) are ca. \$10.00/mol for CF_3CO_2H and ca. \$630/mol for CF_3I. From PCR: ca. \$8.50/mol for CF_3CO_2H, ca. \$323/mol for CF_3I.