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METAL VAPOR SYNTHESIS OF TRIFLUOROMETHYL-GROUP III COMPOUNDS

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Summary

Tris(trifluoromethyl)thallium, $Tl(CF_3)_3$, as well as other less defined trifluoromethyl-Group III compounds have been prepared for the first time by condensing metal atoms with trifluoromethyl radicals on a cryogenic surface. The unusually reactive nature of several of the products necessitated that a very unique and elaborate metal-atom reactor be designed and constructed which would allow the isolation of the products at sub-ambient conditions.

Introduction

Considerable effort has been directed towards synthesizing trifluoromethyl compounds of the Group III elements aluminum, gallium, indium and thallium in our laboratory. Prior to this work, the preparation of these compounds had not been successful even though trimethyl-aluminum, -gallium, -indium and -thallium derivatives have been known for many years. Our curiosity and interest in the trifluoromethyl analogues of these elements has been spurred in part by the proven usefulness of the methyl compounds. Trimethylaluminum, for instance, has many uses as a synthetic reagent; most notable being perhaps its use as an alkylating agent. A similar reagent capable of substituting trifluoromethyl groups onto metals would also be important.

If formed, one can expect the trifluoromethyl compounds of the Group III elements to be exceedingly strong Lewis acids. One can expect the trifluoromethyl compounds to be less stable than the corresponding methyl complexes since the very electronegative CF_3 ligand should increase the electron deficiency (or acidity) of the metal center. The added acidity resulting from the presence of the trifluoromethyl ligand should increase the likelihood that the complex may abstract a halogen from a chlorinated solvent, a well known reaction for Group III complexes, or that the metal may abstract a fluorine from a trifluoromethyl group. This latter reaction can be unimolecular giving rise to a metal fluoride or it may be bimolecular. Unlike the

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Lewis acid trimethylaluminum, trifluoromethylated metals such as aluminum presumably can not be stabilized by forming bridging alkyl groups (a bonding mode not known for the trifluoromethyl ligand). Fortunately, this electron deficiency can be reduced by forming 1/1 adducts with bases such as trialkylphosphines. In the absence of a donor ligand or self association, one would expect tris(trifluoromethyl)thallium, the weakest Lewis acid, to be the most stable and the stability to decrease in the following order: Tl > In > Ga > Al [1]. Hence our initial efforts were directed towards preparing tris(trifluoromethyl)thallium.

A logical synthetic route to these compounds was our metal vapor/free radical chemistry which we first reported in 1979 [2]. This technique involves the reaction of metal atoms with radicals on a liquid nitrogen cooled surface. The radicals are formed in a low temperature glow discharge of a gaseous species with a symmetrical structure having a relatively weak central bond. For example, trifluoromethyl radicals are produced in a hexafluoroethane plasma. The initial reactions were carried out in the reactor shown in Fig. 1. These experiments demonstrated that trifluoromethyl-Group III compounds could be made and that tris(trifluoromethyl)thallium, as predicted, is a stable compound while tris(trifluoromethyl)indium decomposes at temperatures near −20 °C. The gallium and aluminum compounds exhibited even less stability. An equally interesting phenomenon was also observed which appears to be fairly unique to these metals. The reaction products obtained not only contained trifluoromethyl substitution, but a

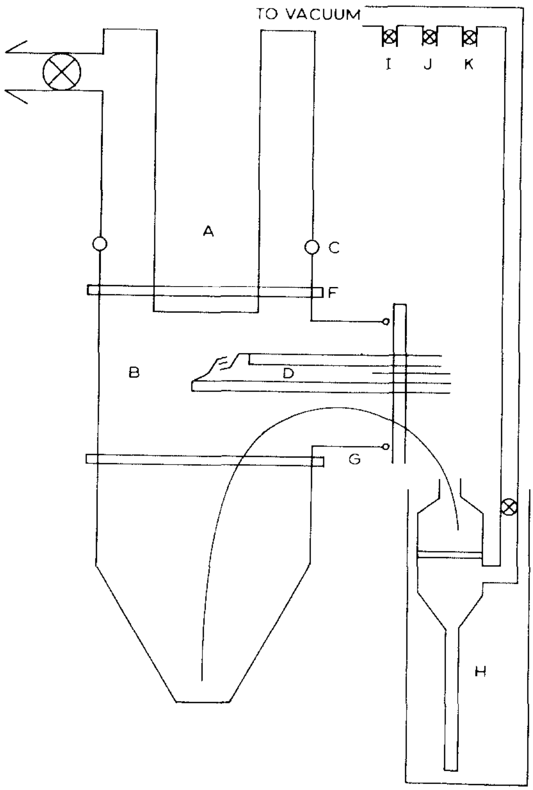

Fig. 1. Reactor type I for low temperature isolation of unstable alkylmetals.

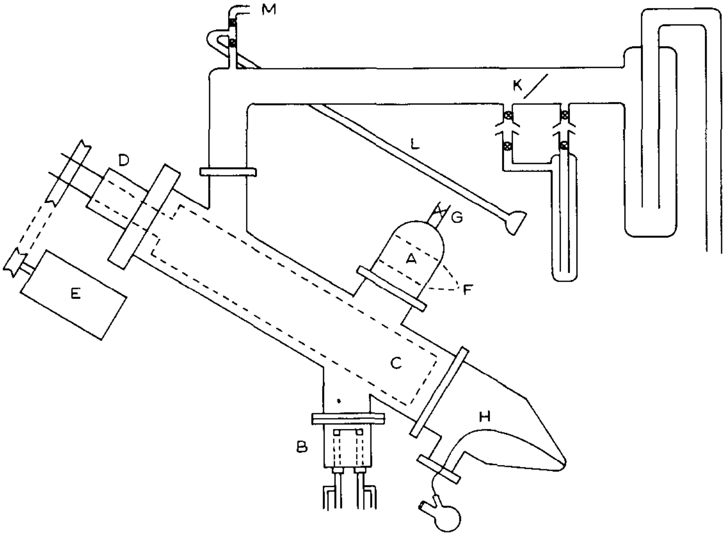

Fig. 2. Rotating cold finger reactor (position I).

significant number of pentafluoroethyl groups and higher oligomers were also substituted on the metals. In fact, it became necessary to build a second reactor, the rotating cold finger reactor (shown in Fig. 2), in order to eliminate the many by-products so that a pure compound could be made and unequivocally characterized.

Experimental

Materials, analyses and physical measurements

The metals used were purchased from Alfa Inorganics and were used without further purification. The hexafluoroethane was dielectric grade DuPont Freon 116. The tungsten baskets used for vaporizing the metals were obtained from R.D. Mathis Co. Radio frequency power was obtained from a Tegal Corporation 100W RF generator with matching network. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York. Infrared spectra were obtained with a Beckman IR-20A spectrometer utilizing KBr disk samples. ^{19}F NMR spectra were recorded using a Bruker WH-90 spectrometer with low temperature capabilities. Mass spectra were obtained with a Bell and Howell Model 21-490 mass spectrometer.

Description of apparatus

Two different reactors were used in preparing the compounds reported. A stationary cold finger reactor (Fig. 1) and a rotating cold finger reactor (Fig. 2). The stationary cold finger reactor consists of a Pyrex cold finger (A) separated from a Pyrex reactor base (B) with a Viton O-ring (C) between two 100 mm O-ring connectors. The radio frequency power is capacitively coupled to the reactor by two metal bands (F and G). A one-half inch Plexiglas plate containing the water-cooled electrical feedthroughs (D), the gas inlets, and a feedthrough for a cannula, is sealed to the reactor base with a 75 mm O-ring connector. The high current electrodes used for resistively heating tungsten baskets were fed through the Plexiglas plate using Cajon O-ring seals which were drilled out in order to accommodate the 1/4″ feedthroughs.

A 18 gauge cannula was used to transfer a low temperature solution containing the product from the reactor into the filtering apparatus. This apparatus consisted of a 5 mm medium wall NMR tube (H) fused onto a 30 mm course filtering frit. A 12 mm tube was attached directly beneath the frit and was used for pumping off the low temperature solvent. If needed, a deuterated NMR solvent could be introduced through inlet (I). A mercury manometer and a thermocouple gauge were attached to inlets (J) and (K) for monitoring the pressure. A one liter dewar containing a frozen slush was used to keep the NMR tube and frit at the desired temperature.

The rotating cold finger reactor (Fig. 2) contained a glass bell jar (A) in which the radicals are produced and a metal evaporation source (B) (routinely metals were resistively heated using the brass base (B) shown in Fig. 2; however, an electron gun or an induction heater could also be attached to the reactor and be used as the source of metal atoms). The metal and radicals were codeposited on a stainless steel cold finger (C) which was spinning at a rate of approximately 200 revolutions per minute. A high vacuum rotating seal (D) was used to make a vacuum tight seal between the cold finger and the rest of the stainless steel reactor. A variable speed motor (E) was used to rotate the cold finger. Two stainless steel bands (F) were used to capacitively couple the radio frequency power to the plasma while the plasma gas entered through inlet (G). A second glass container (H) containing a 75 mm side arm was used for recovering nonvolatile products. An 18 gauge needle passing through a Plexiglas plate on the side arm was used to transfer solutions from the reactor into a collection flask.

The pumping system used consisted of a roughing pump and a diffusion pump. Two glass traps were placed between the reactor and the pumping system. The trap closer to the pump, and larger of the two was cooled with liquid nitrogen to aid in evacuating the reactor and to protect the products from possible contamination with pump oils. The second trap was cooled with liquid nitrogen when the reaction was completed and was used to trap out the volatile reaction products. This was accomplished by closing the butterfly valve (K) and by allowing the cold finger to warm.

The recovery of nonvolatile products, such as $Tl(CF_3)_3$, from the reactor was simplified by mounting the entire apparatus on a rotating aluminum lattice which rotated about a bearing. By rotating the lattice to a position in which the cold finger was perpendicular to the floor (Fig. 3), the frozen matrix could be dropped into the glass bottom of the reactor (H). Once in the bottom of the reactor, the compound can be transferred into a flask via normal Schlenk techniques. A monometer (L) and a nitrogen inlet (M) were attached to the reactor and were used when transferring solutions from the reactor.

General procedure

With the tungsten basket filled with the desired amount of metal, the reactor is assembled and evacuated. The cold finger is cooled by filling with the liquid nitrogen and the gaseous radical precursor, hexafluoroethane, is added at a rate between 1 and 2 mmol/min. The radio frequency power is set at approximately 50 W and the metal is slowly evaporated. When the reaction is complete, the reactor is warmed and the product is isolated and a yield based on the amount of metal evaporated is calculated.

The reaction of thallium vapor with trifluoromethyl radicals

Approximately 1.0 g of thallium was vaporized in a 3 h reaction from an aluminum oxide coated tungsten basket and cocondensed with plasma produced trifluoromethyl radicals using the reactor shown in Fig. 1. Upon completion of the reaction, the cold finger was warmed and the unreacted hexafluoroethane and plasma catenation products were vacuum distilled from the reactor. The reactor was brought into an inert atmosphere box. Approximately 0.68 g of a white tacky solid were removed and extracted with CH_2Cl_2 to give 360 mg of a pale-yellow oil. Hydrolysis of a small portion of the oil using dilute aqueous NaOH gave both CF_3H and C_2F_5H in a ratio of 4 to 1 as well as smaller amounts of C_3F_7H.

Fourier transform ^{19}F NMR gave several peaks in the trifluoromethyl substituted metal region (-10 to $+80$ ppm) (see Table 1). Strong trifluoromethyl resonances (multiplets) were seen at $+16$, $+21$, $+44$ and $+52$ ppm, suggesting that several different trifluoromethyl groups were present in the mixture. Careful analyses of the spectrum using a 20 ppm sweep width revealed that each multiplet observed in the trifluoromethyl substituted metal region of the spectrum consisted of four resonances, thus giving a total of sixteen lines. Detailed integration has shown that these lines correspond to four different trifluoromethyl resonances each of which couple with the ^{203}Tl and ^{205}Tl isotopes which have a nuclear spin of 1/2. Since the two thallium isotopes have slightly different coupling constants, each resonance is split into two doublets or four lines. Thus, the resonances observed near $+16$ ppm as well

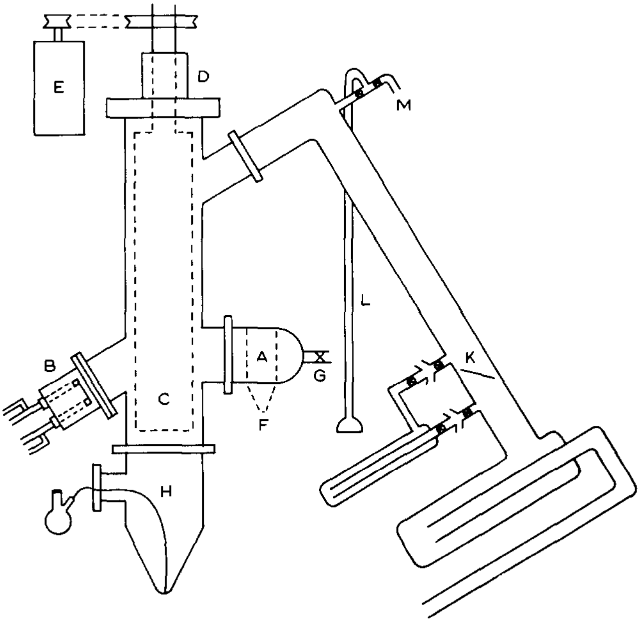

Fig. 3. Rotating cold finger reactor (position II).

as +52 ppm correspond primarily to the major product, $Tl(CF_3)_3$, which has a ^{19}F chemical shift of +34.1 ppm with $J(^{19}F{-}Tl)$ 2957 Hz. In addition to the trifluoromethyl peaks, resonances were observed between +75 and +90 ppm from $CFCl_3$. There was no spectroscopic evidence for a bridging fluoride nor a bridging trifluoromethyl group.

The product mixture, when dissolved in CH_2Cl_2 and allowed to stand at room temperature overnight in an inert atmosphere, gave small light amber colored crystals which were shown to be $Tl(CF_3)_3$ (see below). No attempt was made to further separate the various by-products formed in the reaction. Presumably, the additional peaks observed in the trifluoromethyl region of the NMR spectra were due to compounds such as $Tl(CF_3)_2(C_2F_5)$, $Tl(CF_3)(C_2F_5)_2$, and $Tl(CF_3)(C_2F_5)(C_3F_7)$, etc. Hydrolysis of a crystal with aqueous NaOH gave only CF_3H. Infrared analysis of the crystalline product (KBr disk) gave adsorptions at 1300s, 1170vs, 1010vs, 905m and 715w cm^{-1}. A ^{19}F NMR of the product dissolved in CD_2Cl_2 showed only a doublet at +34.1 ppm from external $CFCl_3$ with $J(Tl{-}F)$ 2957 Hz. ^{205}Tl NMR showed a ten line multiplet at 115, 752, 800 Hz (200 MHz ^1H spectrometer) with $J(Tl{-}F)$ 2960 Hz. Mass spectral analysis of a crystal gave a spectrum consistent with $Tl(CF_3)_3$. Peaks were seen for CF_3^+ m/e 69^+ (48%), Tl^+ (100%), CF_3Tl^+ (13%), $C_2F_6Tl^+$ (5.5%), and $C_3F_8Tl^+$ (1.6%). The parent ion, $(CF_3)_3Tl^+$, was not seen.

The compound, tris(trifluoromethyl)thallium, is initially very soluble in CH_2Cl_2 and $CHCl_3$, but drops out of solution upon standing. It is moderately soluble in diethyl ether, benzene, and toluene and is insoluble in pentane. The compound begins to decompose at 100 °C; however, if heated rapidly (10 °/min) a melting point between 135 and 140 °C is observed. The yield obtained for $Tl(CF_3)_3$ varied from 10 to 20% depending on many variables including the metal evaporation rate, the plasma gas pressure, the distance between the metal source and the cold finger, and the radio-frequency power level.

$Tl(CF_3)_3$, when mixed with triethylphosphine at room temperature, gives rise to a light brown compound. An empirical formula of $Tl(CF_3)_3 \cdot PEt_3$ has been assigned on the bases of weight-gain data. The new compound decomposes before it has sufficient vapor pressure to sublime onto a cold finger and lacks sufficient stability (and volatility) to allow its mass spectrum to be recorded. The compound gave a ^{19}F NMR spectra which was essentially identical to that of $Tl(CF_3)_3$ with the exception of a slight broadening of the fluorine resonances due to $^{19}F{-}^{31}P$ interactions. Typically, F–P spin–spin coupling constants of several Hz are observed for phosphine substituted trifluoromethyl containing organometallic complexes.

TABLE 1

^{19}F NMR OF THALLIUM CF_3 COMPOUNDS: $Tl(CF_3)_x(C_2F_5)_y(C_3F_7)_z$

Compound	δ(ppm) (J(F–Tl) (Hz))		
	CF_3	$C\mathit{F}_3CF_2$	$CF_3C\mathit{F}_2$
$Tl(CF_3)_3$	34.1 (2957)		
$Tl(CF_3)(C_2F_5)_2$?	33.8 (2964)	83.7 (74.6)	107.7 (2034)
$Tl(CF_3)_2(C_2F_5)$?	32.8 (2041)	84.6 (34.0)	111.2 (1506)
$Tl(CF_3)(C_2F_5)(C_3F_7)$?	33.0 (2068)		

The reaction of indium vapor with trifluoromethyl radicals

Slightly more than one gram of indium was vaporized from an aluminum oxide coated tungsten basket in a typical 3 h reaction. Following the reaction, the cold finger was quickly warmed with air and the frozen hexafluoroethane matrix dropped to the bottom of the reactor which was held at −78 °C with a dry ice/acetone slush. The hexafluoroethane was vacuum distilled from the reactor at −78 °C leaving behind the reaction products which were dissolved in 20 ml of diethyl ether. The product containing solution was then quickly transferred into a −78 °C filtering apparatus attached to an NMR tube using Schlenk techniques. The ether was removed by prolonged pumping on the sample at −78 °C. The ether-free products were then dissolved in a small amount of CH_2Cl_2-d_2 and the fluorine NMR of the products was recorded at −78 °C. Two main trifluoromethyl resonances at +41.9 and 42.5 ppm (vs. $CFCl_3$) were seen. Upon warming the tube from −40 to −20 °C, the compounds were shown to decompose uniformly as indicated by the disappearance of the trifluoromethyl resonances.

The reaction of indium vapor with trifluoromethyl radicals and triethylphosphine

A reaction similar to the one described for preparing the unstable trifluoromethylindium compounds was carried out. However, upon completion of the reaction, about 1 ml of triethylphosphine was condensed into the reactor along with 15 ml of diethyl ether prior to warming the matrix. Upon vacuum distilling the hexafluoroethane from the reactor, a cloudy reddish-brown solution remained which was stable at room temperature. Hydrolysis of a small portion of the sample gave significant amounts of CF_3H and C_2F_5H in a ratio of 2/1. Fourier transform NMR spectra gave very broad peaks in three different regions. The first absorption was between +35 and +50 ppm from $CFCl_3$ (the "normal" trifluoromethyl substituted metal compound region). The second region was between +75 and +90 ppm from $CFCl_3$ while the third was between +120 and +150 ppm from $CFCl_3$. The estimated areas under the peaks were about the same in all three regions.

Attempts to separate and purify the individual products were unsuccessful. Recognizing that the fluorine resonance associated with a trifluoromethyl ligand bonded to a metal as well as the methylene fluorine resonance typically occur within a narrow and usually "clean" portion of the fluorine spectrum, one can postulate that the three peaks were due to trifluoromethyl resonances, methylene and methyl resonances of perfluoroethyl groups and perhaps even indium fluorides (+120 to +150 ppm). Cooling the solution to −80 °C had no effect on the spectrum. The mass spectrum of the sample gave only triethylphosphine and fluorocarbon fragments. Elemental analysis of a sample shown to have CF_3 and C_2F_5 ligands in a 1.85 to 1 ratio gave C, 18.1; H, 2.85; F, 37.7; P, 5.17%.

The reaction of gallium with trifluoromethyl radicals

Approximately 0.5 g of gallium was vaporized from an aluminum oxide coated tungsten basket over a 3 h period and the reaction with plasma produced trifluoromethyl radicals. Separation and isolation of the trifluoromethylgallium compounds at −78 °C were unsuccessful owing to their lack of stability at that temperature. However, the addition of triethyl phosphine to the matrix prior to warming allowed the isolation of a mixture of trifluoromethyl containing gallium compounds which were stable at room temperature. Hydrolysis of a small portion of the sample gave

CF_3H and C_2F_5H in a 3/1 ratio. A fluorine NMR of the product mixture dissolved in CH_2Cl_2-d_2 gave four different resonances between +40 and +55 ppm which is in the region of the fluorine spectra which one would expect a fluorine resonance for a trifluoromethyl substituted metal compound. No attempt was made to obtain a pure $Ga(CF_3)_3PEt_3$ compound; however, it is believed that the product mixture closely parallels that obtained for indium.

The reaction of aluminum with trifluoromethyl radicals

The reaction of aluminum with trifluoromethyl radicals did not give a compound which was stable enough to be isolated using the low temperature techniques. However, several unstable trifluoromethylaluminum compounds could be trapped via the addition of triethylphosphine at low temperatures. Owing to the complexity of the mixture obtained, the isolation and characterization of the individual products was not pursued.

The preparation of tris(trifluoromethyl)thallium in the rotating cold finger reactor

Pure tris(trifluoromethyl)thallium, free of the many mixed trifluoromethyl and pentafluoromethyl by-products, could be prepared in the rotating cold finger reactor. Approximately 0.5 g of thallium was slowly vaporized from an aluminum oxide coated tungsten basket placed in the rotating cold finger reactor. After 3 h, the heater and plasma were turned off and the reactor was rotated to the vertical position (Fig. 3). Approximately 15 ml of dry CH_2Cl_2 were condensed onto the cold finger (as it turned) and the matrix was dropped into the glass bottom of the reactor by warming the cold finger with air. A −131°C bath (pentane slush) was placed around the bell jar containing the product which prevented the CH_2Cl_2 from vacuum distilling from the reactor as the hexafluoroethane was trapped out in the liquid nitrogen cooled trap. The reactor was then pressurized with about 500 mm of dry nitrogen and the CH_2Cl_2 solution was allowed to warm to room temperature while being stirred continuously. The pressure was monitored closely so that it would not rise above one atmosphere during the warm-up procedure. After warming to room temperature, the stopcock on an evacuated external flask used for collecting the product was opened and the solution containing the $Tl(CF_3)_3$ product was siphoned into the flask. Once in the flask, a portion of the compound was transferred into a NMR tube while the remaining compound was placed in a hydrolysis flask in an inert atmosphere box. The compound gave only CF_3H upon hydrolysis and possessed a NMR, IR, and mass spectrum identical to the authentic sample previously characterized as being $Tl(CF_3)_3$. A yield of approximately 25% was typically obtained in a 3 h reaction.

Discussion

Experimental evidence has been obtained which suggests that only one of the trifluoromethyl-Group III compounds, $Tl(CF_3)_3$, can be prepared and isolated in the pure form. It is believed that other compounds, such as $Ga(CF_3)_3$ and $In(CF_3)_3$ can be synthesized using the metal vapor/free radical approach, yet they require the addition of a coordinating ligand such as triethylphosphine in order to form a complex stable at room temperature. Results such as these are not at all surprising since a complex containing a bridging trifluoromethyl group has no precedence in organometallic chemistry. Bonding schemes which employ bridging alkyl groups greatly stabilize compounds such as $Al_2(CH_3)_6$. $Tl(CF_3)_3$, like $Tl(CH_3)_3$, evidently exists as a monomer which is stable at room temperature.

The many pentafluoroethyl substituted by-products obtained when these metals were treated with the hexafluoroethane plasma came as an initial surprise. The reactions of mercury, bismuth, tellurium and tin, just to mention a few, with hexafluoroethane plasmas produces the completely substituted trifluoromethyl compounds as the major products [2]. This provides indirect evidence that trifluoromethyl radicals are primarily generated in the plasma when relatively low radio frequency power is employed (< 100 W). Further indirect evidence suggesting that the plasma provides a selective source of trifluoromethyl radicals was obtained by treating mercury vapor with trifluoromethyl and pentafluoroethyl radicals generated in a perfluoropropane glow discharge. A product mixture containing 25% $Hg(C_2F_5)_2$, 50% $Hg(CF_3)(C_2F_5)$, and 25% $Hg(CF_3)_2$ was obtained [3]. Assuming that bond cleavage in perfluoropropane leads to equal concentrations of $^{\cdot}CF_3$ and C_2F_5 radicals, the observed distribution of mercury products could be anticipated if the two radicals react with mercury at similar rates. Since the mercury did not react preferentially with the trifluoromethyl radical and since the reaction of mercury with a hexafluoroethane plasma gave only $Hg(CF_3)_2$, one can deduce that the hexafluoroethane plasma, void of any side reactions initiated by the vaporizing metal, can be used as a clean source of trifluoromethyl radicals.

In the course of conducting the experiments which led to the eventual isolation of $Tl(CF_3)_3$, it was observed that the ratio of CF_3 to C_2F_5 substitution on the thallium was markedly affected by the distance between the metal vapor source and the cold finger. More specifically, by decreasing the distance, i.e., limiting the amount of gas phase interactions between the metal and the radicals, the number of pentafluoroethyl substituents decreased significantly while a concomitant increase in the degree of trifluoromethyl substitution was noted. At a distance of approximately 1/2 inch or less a 10 to 1 ratio of CF_3/C_2F_5 could be routinely obtained. It became apparent from these experiments that the reaction which resulted in the formation of the by-products was a gas phase reaction and was not one which was occurring in the matrix at $-196\,°C$. To circumvent this objectionable reaction, a reactor was designed which totally eliminated the gas phase interactions between the metal atoms and the trifluoromethyl radicals, hence the rotating cold finger reactor was constructed.

The identification of the by-product producing reaction was difficult to ascertain with any degree of certainty. Three gas phase reactions were considered as potential problems. The first mechanism involves the insertion of thallium into hexafluoroethane to give a perfluoroethyl substituted thallium compound.

$$Tl_{(g)} + C_2F_6 \rightarrow FTlC_2F_5 \tag{1}$$

$$FTlC_2F_5 + {}^{\cdot}CF_3 \rightarrow FTl(C_2F_5)CF_3 \tag{2}$$

Although a fluoride substituted trifluoromethylthallium compound has not been identified, a large percentage of the products formed were insoluble in common organic solvents and were believed to be fluoride substituted products. The divalent thallium(II) complex (eq. 1) could dimerize to give a species containing two bridging fluoride ions or it could add another alkyl radical (eq. 2) to form a mixed thallium(III) complex. Metal atom oxidative addition reactions are very common [4]; however, the oxidative addition of a metal into a carbon–fluorine bond is quite fast [5]. By treating thallium atoms with hexafluoroethane in the absence of the radio frequency plasma, it was shown that the thallium probably does not insert since only hexafluoroethane and unreacted thallium metal were recovered following the reaction.

A second mechanism considered for generating pentafluoroethyl substituted thallium compounds involves the gas phase reaction of excited state thallium with CF_3 radicals.

$$Tl^{\star} + n\ CF_3 \rightarrow Tl^{\star}(CF_3)_n \qquad (3)$$

Electrons in the hexafluoroethane plasma have kinetic energies ranging from low values up to and slightly above the energy required for breaking the carbon – carbon bond of the gas (2.5 to 3.1 eV) [6]. The energy required to populate the first spin allowed excited state for thallium is only 2.32 eV [7]. Although this energy is low enough to be easily accessible with the plasma, it is greater than the average thallium–carbon bond strength of 36 kcal/mol (1.51 eV) [8]. Therefore, if radicals react with excited state metal, it is quite likely that the complex formed will decompose as it relaxes to the ground state. The decomposition does not necessarily generate a CF_3 radical and an unsaturated metal, but could relax by channeling the excess energy through suitable vibrational modes of the molecule giving rise to the products seen in the typical thermal decomposition reactions, i.e., difluorocarbene and thallium fluorides.

To test the second hypothesis a slight modification of the reactor shown in Fig. 1 was used. A metal screen was placed below the evaporization crucible and acted as a separator between the metal and the plasma gas. The screen, when connected to an earthground, confined the plasma to the area beneath the screen while allowing the reactive trifluoromethyl radicals to pass through and condense on the cold finger. Since the thallium metal was outside of the plasma region it presumably remained in its ground electronic state. Separation and characterization of the products in the usual manner showed that excited state metal was not a problem (or at least not the only problem) since the product distribution closely resembled that acquired in a normal plasma reaction.

A third and final mechanism to be considered as the by-product forming reaction involves the thermal decomposition of thallium trifluoromethyl compounds to give difluorocarbene which may then insert into thallium–carbon bonds or it may couple with a $^{\cdot}CF_3$ radical to give a C_2F_5 radical (eq. 4 and 5).

$$Tl(CF_3)_n \rightarrow FTl(CF_3)_{n-1} + :CF_2 \qquad (4)$$

$$:CF_2 + CF_3 \rightarrow C_2F_5 \qquad (5)$$

Although $Tl(CF_3)_3$ is stable at room temperature, during the course of the reaction unstable trifluoromethylthallium complexes are generated. For instance, unstable $TlCF_3$ as well as $Tl(CF_3)_2$ intermediates are formed which then add a second or third radical to give the stable $Tl(R)_3$ compounds. If the mono- and di-substituted thallium intermediates form in the gas phase, it is likely that they would decompose prior to reaching the cold finger. To date, all of the trifluoromethylmetal compounds known give a metal fluoride and difluorocarbene (eq. 6) when heated to their decomposition temperatures.

$$Tl(CF_3)_n \rightarrow FTl(CF_3)_{n-1} + :CF_2 \quad n = 1,2 \tag{6}$$

Similarly, difluorocarbene was observed by Klabunde and coworkers while preparing CF_3ZnI via a metal atom route [9]. Presumably a reaction such as this is responsible for the low yields which are obtained when the stationary cold finger reactor is used.

Acknowledgement

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