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# REACTIVITY OF THE METAL–METAL BOND
## IX. EXCHANGE REACTIONS INVOLVING METAL–METAL BOND CLEAVAGE

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## SUMMARY

Attempts to insert difluorocarbene into tin–manganese, germanium–manganese, tin–iron, and tin–tungsten bonds were unsuccessful. Surprisingly, thermal reactions of trimethyltrifluoromethyltin, a good source of difluorocarbene, with $(CH_3)_3MMn(CO)_5$ led to the formation of $CF_3(CH_3)_2SnMn(CO)_5$ and $(CH_3)_4M$ ($M = Ge$ or Sn). This type of exchange of (alkyl-metal)groups by metal–metal bonded compounds has not been observed previously.

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## INTRODUCTION

During investigations of the chemical behavior of metal–metal bonds, we have attempted to insert difluorocarbene into a number of metal–metal bonds. Seyferth and co-workers[1] have reported insertions of dihalocarbenes, $CCl_2$ and/or CClBr, generated by thermal decomposition of trihalomethylmercurials, into tin–tin, silicon–mercury and germanium–mercury bonds. In this work, thermal decomposition of trimethyl(trifluoromethyl)tin[2] was used as the source of difluorocarbene and unusual exchange reactions have been observed.

## EXPERIMENTAL

Standard high vacuum techniques were used for the handling of volatile compounds. Most of the solid compounds in this work were sufficiently volatile that sublimation was employed for purifications. Infrared spectra were determined on Beckman IR-7 and IR-10 spectrometers. Nuclear magnetic resonance spectra were determined on Varian Associates A-60 and HA-100 spectrometers. Proton spectra were run at 60 MHz or 100 MHz using cyclohexane or chloroform as solvent and reference. Fluorine-19 spectra were run at 94.1 MHz using fluorotrichloromethane as solvent and reference. Analyses were determined by A. B. Gygli, Toronto, Ontario, or Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y.

The syntheses of the metal–metal bonded derivatives used in this work have all been reported previously[3] and no significant changes were made in the preparations.

### *Hexamethylditin and trimethyl(trifluoromethyl)tin*

Hexamethylditin and trimethyl(trifluoromethyl)tin were prepared in good yield by the method reported by Clark and Willis[2] except that the hexamethylditin was not purified prior to reaction with trifluoroiodomethane. The trimethyl(trifluoromethyl)tin was purified by trap to trap distillation through −23°, −45°, −78°, and −196° traps. Most of the trimethyltin iodide was stopped in the −45° trap, the excess $CF_3I$ was in the −196° trap, and the $(CH_3)_3SnCF_3$ (contaminated by $(CH_3)_3SnI$) was in the −78° trap. All but a trace of the $(CH_3)_3SnI$ was removed by a second pass through a −45° trap.

### *Reactions with trimethyl(trifluoromethyl)tin*

Reactions with trimethyl(trifluoromethyl)tin were carried out in small Carius tubes or thick-walled Pyrex NMR tubes. Excess $(CH_3)_3SnCF_3$ was used as the solvent and the tubes were shaken in a small oven. If shaking was not employed, extensive decomposition occurred on the walls of the tube. When reactions were done in NMR tubes, the tubes were inverted and centrifuged prior to running the spectra to remove suspended solids, mainly trimethyltin fluoride. A small amount of cyclohexane was added to the samples to provide an internal reference from which chemical shifts and relative integrals could be calculated. The infrared spectra of the $CF_3(CH_3)_2Sn$–R compounds all exhibit characteristic C–F stretching bands at 1040 and 1130 $cm^{-1}$ and there is virtually no difference from one compound to another.

*(Trimethylstannyl)pentacarbonylmanganese* (2.071 g, 5.75 mmoles) and $(CH_3)_3SnCF_3$ (1.666 g, 7.10 mmoles) were sealed in a small Pyrex Carius tube and shaken at 115° for 18 h. The tube was frozen in liquid nitrogen, opened into the vacuum line, and fractionated through −23°, −45°, −95°, and −196° traps. A trace of CO was detected upon opening the tube and the −196° trap contained 20 mg of a mixture of $C_2F_4$, cyclo-$C_3F_6$, and $CF_3H$ which were identified from the infrared spectrum[2,4]. The −95° trap contained 1.55 g of material; this was shown to be 0.75 mmoles of tetramethyltin and 6.05 mmoles of $(CH_3)_3SnCF_3$ from calculations of the relative amounts shown in the NMR spectrum. The −45° trap was empty but the −23° trap contained 1.381 g of material which, from the NMR spectrum was shown to be 0.44 mmoles of $CF_3(CH_3)_2SnMn(CO)_5$, together with 3.34 mmoles of unreacted $(CH_3)_3SnMn(CO)_5$. The involatile residue was extracted with diethyl ether to give, upon evaporation of the ether, $(CH_3)_2Sn[Mn(CO)_5]_2$ (0.39 g, 0.7 mmoles). The remaining material was extracted with warm methanol to yield trimethyltin fluoride (0.123 g, 0.67 mmoles). Approximately 40 mg of an intractible residue was left in the tube. $CF_3(CH_3)_2SnMn(CO)_5$ was isolated in pure form from a reaction in which $(CH_3)_3SnMn(CO)_5$ was heated with a very large excess of $(CH_3)_3SnCF_3$ at 80° overnight and was identified by comparison of its spectrum with that of an authentic sample prepared from $(CH_3)_2CF_3SnCl$ and $NaMn(CO)_5$[5]. (Found: C, 23.87; H, 1.85; F, 13.65. $C_8H_6F_3O_5MnSn$ calcd.: C, 23.28; H, 1.46; F, 13.80%.) $(CH_3)_2Sn[Mn(CO)_5]_2$ was identified by comparison of melting point, NMR and infrared spectra with literature values[6,7].

*(Trimethylgermyl)pentacarbonylmanganese* (0.931 g, 2.98 mmoles) and $(CH_3)_3SnCF_3$ (2.756 g, 11.75 mmoles) were sealed in a small Pyrex Carius tube and heated at 120° for 18 h. The tube was cooled in liquid nitrogen, opened into a vacuum and fractionated through −23°, −78°, and −196° traps. A trace of noncondensable gas

(presumably CO) was produced and the −196° trap contained (by infrared[2,4]) a mixture of $C_2F_4$, cyclo-$C_3F_6$ and $CF_3H$ with a trace of $(CH_3)_4Ge$. The −78° trap contained 1.97 grams of material, which was shown, from calculations on the relative intensities in the NMR spectrum, to be 2.14 mmoles of tetramethylgermane and 7.22 mmoles of $(CH_3)_3SnCF_3$. The −23° trap contained 0.646 g of material which, by infrared and NMR, was shown to be $CF_3(CH_3)_2SnMn(CO)_5$ contaminated with unreacted $(CH_3)_3GeMn(CO)_5$. Several sublimations at room temperature onto a water cooled cold finger yielded a sample of pure $CF_3(CH_3)_2SnMn(CO)_5$ (0.418 g, 1 mmole). (Found: C, 23.87; H, 1.75; F, 13.65. $C_8H_6F_3O_5MnSn$ calcd.: C, 23.28; H, 1.46; F, 13.80%; m.p. 49°, lit.[5] 49°.) The involatile residue was extracted with hexane which gave, upon evaporation of the hexane, approximately 150 mg of an oily residue which from its infrared spectrum contained carbonyl, methyl–tin, methyl–germanium and C–F groups. The hexane insoluble residue was extracted with hot methanol to yield trimethyltin fluoride (0.36 g, 2 mmoles) and leave an insoluble residue of about 100 mg.

*(Trimethylstannyl)pentacarbonylmanganese* (0.089 g, 0.25 mmoles) and $CF_3(CH_3)_2SnMn(CO)_5$ (0.096 g, 0.23 mmoles) were sealed in a small Pyrex tube and heated at 120° for 24 h. The tube was cooled in liquid nitrogen, opened into a vacuum line, and fractionated through −23°, −78°, and −196° traps. Since the crude reaction product was solid at room temperature it was necessary to heat the tube in hot water in order to melt the product and transfer most of it into the vacuum system. Only a trace of material was found in the −196° trap. The −78° trap contained $(CH_3)_3SnCF_3$ (28 mg, 0.12 mmoles), identified from its gas phase infrared spectrum. The −23° trap contained approximately 60 mg of a mixture of $(CH_3)_3SnMn(CO)_5$ and $CF_3(CH_3)_2SnMn(CO)_5$. The residue in the tube was dissolved in pentane, filtered, and the pentane was slowly removed on the vacuum line, allowing the solution to cool. Before all of the pentane had been removed, the white crystals which had formed were filtered from the cold solution. Upon evaporation of the mother liquor to dryness, a further crop (about 40 mg) of crystals was obtained. From the infrared and NMR spectra this second crop was a mixture of $(CH_3)_3SnMn(CO)_5$, $CF_3(CH_3)_2SnMn(CO)_5$ and $(CH_3)_2Sn[Mn(CO)_5]_2$. The first crop of crystals was pure $(CH_3)_2Sn[Mn(CO)_5]_2$ (45 mg, 0.08 mmoles) identified from its infrared and NMR spectra[6,7]. (M.p. 101°–103°, lit.[7] 102°–104°).

*(Trimethylstannyl)-π-cyclopentadienyldicarbonyliron* (0.739 g) was allowed to react with 0.845 g of $(CH_3)_3SnCF_3$ at 115° overnight and fractionated through −23°, −78°, and −196° traps. The −78° trap contained an almost equimolar mixture of $(CH_3)_3SnCF_3$ and $(CH_3)_4Sn$ which indicates very extensive disproportionation of the tin–iron compounds. The involatile residue was chromatographed on Florisil to give a fraction which by $^1H$ and $^{19}F$ NMR was a mixture of $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ and $CF_3(CH_3)_2SnFe(CO)_2(\pi\text{-}C_5H_5)$. The reaction was repeated on a smaller scale in an NMR tube and the ratio of products indicated that the reaction amounted to a disproportionation of $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)$ to $(CH_3)_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ and $(CH_3)_4Sn$ with a small amount of $CF_3(CH_3)_2SnFe(CO)_2(\pi\text{-}C_5H_5)$ being present.

*(Trimethylstannyl)(π-cyclopentadienyl)tricarbonyltungsten* (631 mg, 1.3 mmoles) and $(CH_3)_3SnCF_3$ (1.252 g, 5.4 mmoles) were heated at 115° for 17 h and fractionated on a vacuum system. A mixture of $(CH_3)_3SnCF_3$ and $(CH_3)_4Sn$ was isolated from the

TABLE I

NMR DATA FOR $CF_3(CH_3)_2SnX$ COMPOUNDS

| X | $\tau(CH_3)$ | $J(^{117}SnCH)$ (Hz) | $J(^{119}SnCH)$ (Hz) | $\delta(CF_3)^a$ | $J(^{117}SnCF)$ (Hz) | $J(^{119}SnCF)$ (Hz) |
|---|---|---|---|---|---|---|
| $CH_3$ | 9.8 | 55 | 58 | 49.3 | 276 | 288 |
| $Mn(CO)_5$ | 9.7 | 46 | 48 | 47.0 | 242 | 253 |
| $Fe(CO)_2(C_2H_5)$ | 9.6 | 47 | 49 | 48.5 | 200 | 209 |
| $W(CO)_3(C_5H_5)$ | 9.6 | 48 | 50 | 47.5 | 210 | 220 |

[a] In ppm from $CFCl_3$.

−78° trap. The less volatile material from the reaction tube was sublimed to give a mixture of $(CH_3)_3SnW(CO)_3(\pi\text{-}C_5H_5)$ and $CF_3(CH_3)_2SnW(CO)_3(\pi\text{-}C_5H_5)$. Attempts to separate the mixture by chromatography failed because most of the material was held firmly on the column when hexane was used as the eluting solvent and both compounds eluted together when more polar solvents were used.

## DISCUSSION

The expected difluorocarbene insertion products are not formed in significant amounts but it is unlikely that this is a result of a lack of thermodynamic stability since similar compounds such as $(CH_3)_3SnCF_2CF_2Mn(CO)_5$ can be isolated even though elimination of $(CH_3)_3SnF$ can easily occur[8].

Reactions of (trimethylstannyl)pentacarbonylmanganese have been studied in detail[5,8] and consequently this compound has been used here. In addition to the fact that there is a good mass balance between total weight of reactants and total weight of products as indicated in the Experimental section, a number of other relevant points should be noted:

(1). More $(CH_3)_3SnMn(CO)_5$ than $(CH_3)_3SnCF_3$ is consumed.

(2). A significant proportion of the $(CH_3)_3SnCF_3$ which does react decomposes to form $(CH_3)_3SnF$ and $[CF_2]$.

(3). When $(CH_3)_3SnMn(CO)_5$ is heated to 130° for 48 h only very slight disproportionation to $(CH_3)_4Sn$ and $(CH_3)_2Sn[Mn(CO)_5]_2$ occurs[8].

(4). When $(CH_3)_3SnMn(CO)_5$ and $CF_3(CH_3)_2SnMn(CO)_5$ are heated together, $(CH_3)_2Sn[Mn(CO)_5]_2$ and $(CH_3)_3SnCF_3$ are formed.

The reaction of $(CH_3)_3GeMn(CO)_5$ with $(CH_3)_3SnCF_3$ produces $CF_3(CH_3)_2SnMn(CO)_5$ and $(CH_3)_4Ge$, so that the germanium–manganese bond must be cleaved. It has been shown that, within experimental error, the dissociation energies of the tin–manganese and germanium–manganese bonds in $(CH_3)_3\text{-}MMn(CO)_5$ ($M = Sn$ or Ge) are the same[9]. This, coupled with other similarities in chemistry[8,10] would imply that the tin–manganese bond is also cleaved.

Our observations may then be summarized by the following reaction, for $M = Sn$ or Ge:

$$(CH_3)_3MMn(CO)_5 + (CH_3)_3SnCF_3 \rightarrow CF_3(CH_3)_2SnMn(CO)_5 + (CH_3)_4M$$

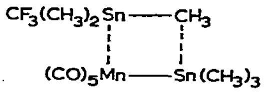
and in the case of the trimethyltin compound, there is the additional reaction:

$$CF_3(CH_3)_2SnMn(CO)_5 + (CH_3)_3SnMn(CO)_5 \rightarrow (CH_3)_2Sn[Mn(CO)_5]_2 + (CH_3)_3SnCF_3$$

In the absence of kinetic data, it is not possible to define the reaction mechanism but some possibilities may be eliminated.

Since it has been shown that metal–metal bonds may ionize in solution[12,13], it is tempting to propose ionic intermediates. However, when $(CH_3)_3GeMn(CO)_5$ is dissolved in $(CH_3)_3SnCF_3$ the infrared spectrum of the carbonyl region is identical to that run in cyclopentane and in particular no band is present which could be assigned to $[Mn(CO)_5]^-$.

A free radical route is not likely because $(CH_3)_3SnCF_3$ is prepared by ultraviolet irradiation of $CF_3I$ and hexamethylditin and must be stable to free radical bond cleavages. Also, if the metal–metal bond were being cleaved homolytically some dimanganesedecacarbonyl would be produced either by radical coupling or reaction of pentacarbonylmagnanese radicals with the $(CH_3)_3SnMn(CO)_5$. The initial step of the reaction may well involve a cyclic transition state such as:



Attempts to achieve the initial objective of inserting difluorocarbene into metal–metal bonds have been unsuccessful. If the temperature is raised to 150° the reaction of $(CH_3)_3$ $SnCF_3$ with metal–metal bonded derivatives produces perfluorocyclopropane in good yield and no compounds resembling carbene insertion products have been observed. The metal–metal bonded compounds either decompose to a tarry residue or are recovered unreacted. If phenyl(trichloromethyl)mercury is used as a source of dichlorocarbene, $(CH_3)_3SnMn(CO)_5$ and $(CH_3)_3SnMo(CO)_3(\pi\text{-}C_5H_5)$ both decompose rapidly with loss of carbon monoxide.

The present reactions, as the first observed instances of metal–metal bonded compounds exchanging (alkyl–metal) groups, apparently illustrate an interesting and unexpected aspect of the reactivity of metal–metal bonds.

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