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CHEMISTRY OF TRIFLUOROMETHYL COMPOUNDS

I. NMR EVIDENCE FOR BIS(TRIFLUOROMETHYL)ZINC AND METHYL(TRIFLUOROMETHYL)ZINC

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Summary

Bis(trifluoromethyl)zinc and methyl(trifluoromethyl)zinc have been identified by ^{19}F and ^{1}H NMR methods. The compounds were formed in the following reactions: (1) dimethylzinc and bis(trifluoromethyl)mercury and (2) dimethylzinc and bis(trifluoromethyl)cadmium.

Introduction

Recently there has been interest in the use of bis(trifluoromethyl)mercury as a source for trifluoromethyl groups [1]. The limitations of bis(trifluoromethyl)mercury in this application have been pointed out [1]. The importance of Group IIB dimethyl compounds as sources of methyl groups is well documented [2] and we felt that Group IIB bis(trifluoromethyl) compounds other than $(CF_3)_2Hg$ would also be trifluoromethyl sources. Very little has been reported concerning the chemistry of the trifluoromethyl compounds of zinc and cadmium *.

Since the work of Dyatkin et al. [4] on the dimethylcadmium/bis(trifluoromethyl)mercury system, no further synthetic utilization of bis(trifluoromethyl)cadmium has been reported. This is surprising since Seyferth [5] has pointed out the possible synthetic applicability of bis(trifluoromethyl)cadmium.

We would like to report here our NMR study on the dimethylzinc/bis(trifluoromethyl)mercury and dimethylzinc/bis(trifluoromethyl)cadmium systems. The new trifluoromethyl species identified by NMR are bis(trifluoromethyl)zinc and methyl(trifluoromethyl)zinc.

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* Attempted preparations of trifluoromethyl-containing zinc and cadmium compounds have been reported in the papers mentioned in ref. 3.

Experimental

Bis(trifluoromethyl)mercury [6] and dimethylzinc [7] were prepared by literature methods. Dimethylcadmium was purchased from Alfa/Ventron Products and used without further purification. Pyridine was distilled from P_2O_5 or BaO and stored over molecular sieves. Bis(trifluoromethyl)cadmium was prepared by reaction of dimethylcadmium (70 mg, 0.5 mmol) with bis(trifluoromethyl)mercury (395 mg, 1.2 mmol) in pyridine (4.0 ml). Removal of all volatile materials by vacuum pumping at room temperature for several days left a light brown residue from the original brown solution. The volatile materials were identified as pyridine, $Hg(CF_3)(CH_3)$ and unreacted $Hg(CF_3)_2$. The light brown residue was identified as bis(trifluoromethyl)cadmium by its ^{19}F NMR spectrum in pyridine solution [4]. The reported ^{19}F and ^1H NMR spectra identified the compound as $Cd(CF_3)_2$ and not $Cd(CF_3)(CH_3)$. No other trifluoromethyl containing compounds were identified in the brown compound by ^{19}F and ^1H NMR spectra. The purity of the compound was determined by mass spectral analysis; no mercury containing compounds were found to be present.

All reactions were run in sealed 4 mm glass tubes. All transfers were made in inert atmosphere or on a vacuum line. NMR chemical shifts are reported vs. $CFCl_3$ for ^{19}F and TMS for ^1H. The reference compound, dissolved in pyridine, was placed externally in the 5 mm NMR tube. ^{19}F NMR spectra were recorded on a Varian EM-390 spectrometer operating at 84.56 MHz and ^1H NMR spectra were recorded on either a Varian EM-390 or Varian EM-360 spectrometer operating at 90 and 60 MHz, respectively. Low temperature spectra were recorded on the Varian EM-390 instrument. The temperature of the reaction was essentially at 34°C, the magnet temperature. The glass tubes were periodically shaken to insure adequate mixing of the components.

A. Dimethylzinc/bis(trifluoromethyl)mercury system

Reaction 1. To a sample of 37.1 mg (0.11 mmol) of bis(trifluoromethyl)mercury in a 4 mm tube was added 0.3 ml of pyridine and 6 mg (0.063 mmol) of dimethylzinc. The tube was cooled to —196°C, sealed in vacuum and then allowed to warm to room temperature. The progress of the reaction was monitored by both ^{19}F and ^1H NMR. Upon immediate mixing, the following compounds were identified by NMR: $Hg(CF_3)_2$, $Hg(CF_3)(CH_3)$, and $Zn(CF_3)(CH_3)$, in a 3/2/2 ratio. Thirty minutes after mixing, four compounds were identified in a 2/2/1/1 ratio: $Hg(CF_3)_2$, $Hg(CF_3)(CH_3)$, $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$. Approximately 8 h after initial mixing, all the $Hg(CF_3)_2$ was consumed, leaving only $Hg(CF_3)(CH_3)$, $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$, in a ratio of 15/1/7. An unidentifiable peak appeared in the ^{19}F NMR spectrum at 37.4 ppm. After 7 days, the ratio of $Hg(CF_3)(CH_3)$, $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$ was 20/1/4.5 and a precipitate began to form in the original red-brown solution. ^{19}F: $Hg(CF_3)_2$: 33.0 ppm, $J(^{199}Hg—F)$ 1290 Hz. $Hg(CF_3)(CH_3)$: 35.6 ppm, $J(^{199}Hg—F)$ 941 Hz. $Zn(CF_3)(CH_3)$: 37.9 ppm. $Zn(CF_3)_2$: 38.0 ppm. ^1H: $Hg(CF_3)(CH_3)$: 0.58 ppm, $J(^{199}Hg—H)$ 145 Hz. $Zn(CF_3)(CH_3)$: —0.32 ppm.

Reaction 2. As in the previous reaction, a sample consisting of 18.6 mg (0.055 mmol) of $Hg(CF_3)_2$, 0.3 ml of pyridine, and 26 mg (0.27 mmol) of $Zn(CH_3)_2$ was prepared. Upon immediate mixing, components identified were

$Hg(CF_3)(CH_3)$ and $Zn(CF_3)(CH_3)$ in 1/1 ratio. Thirty min after mixing, the components identified were $Hg(CF_3)(CH_3)$, $Zn(CF_3)(CH_3)$, and $Hg(CH_3)_2$ in ratio 2/3/2. An hour after mixing, the ratio of the three components was 1/4/2. Three hours after mixing, all the $Hg(CF_3)(CH_3)$ had been converted to $Hg(CH_3)_2$. Low temperature ^1H NMR showed that the proton ratio of $Hg(CH_3)_2$, $Zn(CH_3)_2$, and $Zn(CF_3)(CH_3)$ at equilibrium was 1/3.2/1.5. ^{19}F: $Hg(CF_3)(CH_3)$: 35.6 ppm, $J(^{199}Hg-F)$ 947 Hz, $Zn(CF_3)(CH_3)$: 37.9 ppm. ^1H: $Hg(CF_3)(CH_3)$: 0.58 ppm. $Hg(CH_3)_2$: 0.14 ppm, $J(^{199}Hg-H)$ 101 Hz. $Zn(CF_3)(CH_3)$: −0.39 ppm. $Zn(CH_3)_2$: −0.24 ppm.

Reaction 3. As above, a sample was prepared with 54.5 mg (0.16 mmol) of $Hg(CF_3)_2$, 0.3 ml of pyridine, and 13.4 mg (0.14 mmol) of $Zn(CH_3)_2$. Upon mixing, $Hg(CF_3)_2$, $Hg(CF_3)(CH_3)$, and $Zn(CF_3)(CH_3)$ were present in the red-brown solution in a ratio of 5/5/4. A ratio of 1/1.4/0.1/0.8/0.4 resulted after 1/2 h, corresponding to $Hg(CF_3)_2$, $Hg(CF_3)(CH_3)$, X (unknown), $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$. One hour after initial mixing, the ratio of the five components was 2/5/0.3/2.5/1.5. Formation of a small amount of $Hg(CH_3)_2$ also resulted after 2 h. The ratio of $Hg(CF_3)(CH_3)$ to $Hg(CH_3)_2$ never exceeded 30/1. All the $Hg(CF_3)_2$ has been converted to corresponding products by 2.5 h after initial mixing. The product distribution at this point was 6.1/3/2.5 for $Hg(CF_3)(CH_3)$, $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$. The previously unknown peak had disappeared. At this point, the red-brown solution had turned a muddy brown. ^{19}F: $Hg(CF_3)_2$: 33.0 ppm, $J(^{199}Hg-F)$ 1294 Hz. $Hg(CF_3)(CH_3)$: 35.6 ppm, $J(^{199}Hg-F)$ 944 Hz. X (unknown): 37.6 ppm. $Zn(CF_3)(CH_3)$: 37.8 ppm. $Zn(CF_3)_2$: 38.0 ppm. ^1H: $Hg(CF_3)(CH_3)$: 0.58 ppm, $J(^{199}Hg-H)$ 140 Hz. $Hg(CH_3)_2$: 0.18 ppm. $Zn(CF_3)(CH_3)$: −0.32 ppm.

B. Dimethylzinc/bis(trifluoromethyl)cadmium system *

Reaction 1. Prepared as above was a sample consisting of 37.8 mg (0.093 mmol) of $Cd(CF_3)_2$, 0.2 ml of pyridine, and 6 mg (0.063 mmol) of $Zn(CH_3)_2$. Initial mixing produced a 2/3/1.5 distribution of products in the red-brown solution, corresponding to $Cd(CF_3)_2$, $Cd(CF_3)(CH_3)$, and $Zn(CF_3)(CH_3)$. After 15 min, a distribution of 1/9/0.2/3/2.5 resulted, attributable to the following compounds, $Cd(CF_3)_2$, $Cd(CF_3)(CH_3)$, X (unknown), $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$. The equilibrium mixture after an hour was 1/11/1/2.5/5.6 consisting of $Cd(CF_3)_2$, $Cd(CF_3)(CH_3)$, X (unknown), $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$. After 6 h, the ratio of $Cd(CF_3)_2$ to $Cd(CF_3)(CH_3)$ had changed to 1/22. After several days at room temperature, a 2/1/1 distribution resulted, attributable to $Cd(CF_3)(CH_3)$, $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$. Also present at this point was CF_3H. ^{19}F: $Cd(CF_3)_2$: 30.3 ppm, $J(^{111/113}Cd-F)$ 355/372 Hz. $Cd(CF_3)(CH_3)$: 31.1 ppm, $J(^{111/113}Cd-F)$ 301/316 Hz, X (unknown): 37.2 ppm. $Zn(CF_3)(CH_3)$: 37.8 ppm. $Zn(CF_3)_2$: 38.0 ppm. ^1H: $Cd(CF_3)(CH_3)$: −0.15 ppm, $J(^{111/113}Cd-H)$ 60 Hz. $Zn(CF_3)(CH_3)$: −0.32 ppm.

Reaction 2. Prepared as above was a sample consisting of 12.0 mg (0.029

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* Details concerning the characterization of bis(trifluoromethyl)cadmium will be given in a subsequent paper. Calculated mole for bis(trifluoromethyl)cadmium in the experimental section is based on $Cd(CF_3)_2 \cdot 2py$. For convenience, the cadmium compounds will be referred to as bis(trifluoromethyl)cadmium, $Cd(CF_3)_2$.

mmol) of $Cd(CF_3)_2$, 0.2 ml of pyridine, and 12.1 mg (0.13 mmol) of $Zn(CH_3)_2$. Upon initial mixing, only one peak, attributable to $Zn(CF_3)(CH_3)$, was observed in the ^{19}F NMR spectrum. The ^1H NMR spectrum showed a single, very broad peak. Upon cooling the sample, the broad peak separated into three distinct peaks. The ratio of components at $-30°$ C was 2/2.5/1, corresponding to $Cd(CH_3)_2$, $Zn(CH_3)_2$, and $Zn(CF_3)(CH_3)$. ^{19}F: $Zn(CF_3)(CH_3)$: 37.8 ppm. ^1H: $Cd(CH_3)_2$: -0.16 ppm, $J(^{111/113}Cd{-}H)$ 48 Hz. $Zn(CH_3)_2$: -0.24 ppm. $Zn(CF_3)(CH_3)$: -0.32 ppm.

Reaction 3. As previously, a sample consisting of 24.6 mg (0.06 mmol) of $Cd(CF_3)_2$, 0.2 ml of pyridine, and 6 mg (0.063 mmol) of $Zn(CH_3)_2$ was prepared. Upon initial mixing, four components were identified as $Cd(CF_3)_2$, $Cd(CF_3)(CH_3)$, $Zn(CF_3)(CH_3)$, and $Zn(CF_3)_2$, present in a ratio of 6/10/2/1. After 15 min, the ratio of the four components changed to 1/4/1.1/1. After 30 min, the ratio of the four components was 1/6/1.5/2. At the end of an hour, almost all of the $Cd(CF_3)_2$ had been converted to other products, leaving a ratio of the four components as 1/15/7/5. An unknown peak had appeared in the same amount as $Cd(CF_3)_2$. This unknown peak subsequently disappeared after several days. ^{19}F: $Cd(CF_3)_2$: 30.4 ppm, $J(^{111/113}Cd{-}F)$ 350/366 Hz. $Cd(CF_3)(CH_3)$: 31.1 ppm, $J(^{111/113}Cd{-}F)$ 302/319 Hz. X (unknown): 37.2 ppm.

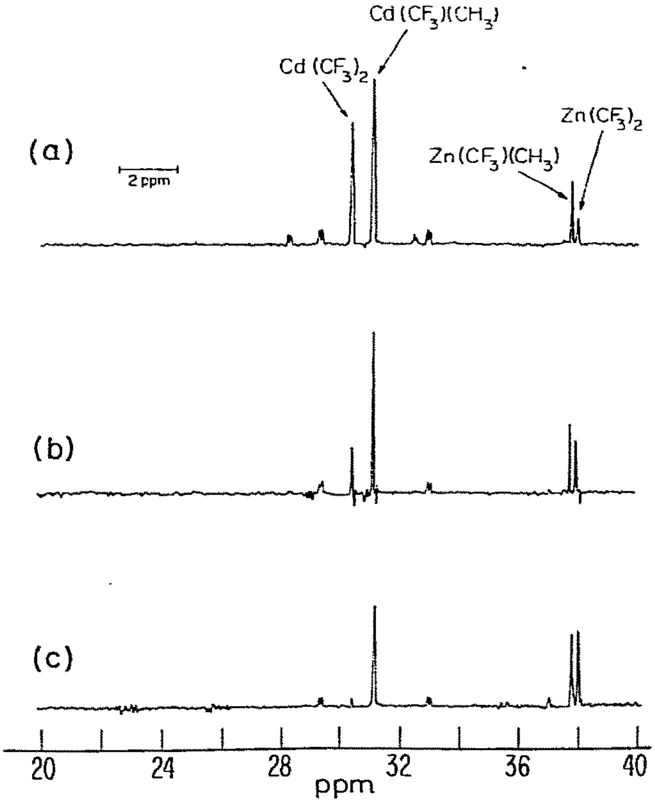

Fig. 1. Dimethylzinc/bis(trifluoromethyl)cadmium system. (^{19}F NMR spectra for reaction 3.) (a) Initial mixing. (b) Fifteen minutes after initial mixing. (c) Thirty minutes after start.

$Zn(CF_3)(CH_3)$: 37.8 ppm. $Zn(CF_3)_2$: 38.0 ppm. ^1H: $Cd(CF_3)(CH_3)$: −0.17 ppm, $J(^{111/113}Cd{-}H)$ 60 Hz. $Zn(CF_3)(CH_3)$: −0.32 ppm (see Fig. 1).

Results and discussion

Identification of the two new compounds, $Zn(CF_3)_2$ and $Zn(CF_3)(CH_3)$, was made through both the ^{19}F and ^1H spectra of the two systems studied. Since both the dimethylzinc/bis(trifluoromethyl)mercury and dimethylzinc/bis(trifluoromethyl)cadmium systems led to the same results in product distribution for bis(trifluoromethyl)zinc and methyl(trifluoromethyl)zinc, it is believed that this is unequivocal evidence for $Zn(CF_3)_2$ and $Zn(CF_3)(CH_3)$.

Identification of $Zn(CF_3)_2$ and $Zn(CF_3)(CH_3)$ was made by comparison of the ^{19}F and ^1H NMR spectra. With the experiments described, one can observe different species increase in intensity as other species decrease in intensity. For example, as the amount of $Hg(CF_3)_2$ decreased, the amount of $Hg(CF_3)(CH_3)$ and $Zn(CF_3)(CH_3)$, assigned to the first new species formed, increased as observed in both the ^{19}F and ^1H NMR spectra. For $Zn(CF_3)(CH_3)$, corresponding ^{19}F and ^1H NMR signals appeared. Further exchange with $Hg(CF_3)_2$ caused $Zn(CF_3)(CH_3)$ to decrease in intensity as $Zn(CF_3)_2$, assigned to the second new species formed, increased in intensity as observed in the ^{19}F NMR spectra. Correspondingly, the ^1H NMR signal diminished for $Zn(CF_3)(CH_3)$.

Since it is well known that the dimethyl compounds of Zn, Cd, and Hg exchange [8], it would not be surprising that the corresponding trifluoromethyl compounds have similar properties. This has been shown to be true in the dimethylcadmium/bis(trifluoromethyl)mercury system [4]. As in all exchange systems, it is expected that the final distribution of products would depend on the initial concentrations of reactants. This is what is found in the two systems reported here, dimethylzinc/bis(trifluoromethyl)mercury and dimethylzinc/bis(trifluoromethyl)cadmium. The rapid exchange between methyl and trifluoromethyl groups produces bis(trifluoromethyl)zinc and methyl(trifluoromethyl)zinc.

Qualitatively it was found that the exchange between dimethylzinc and bis(trifluoromethyl)cadmium proceeded initially much more rapidly than the exchange between dimethylzinc and bis(trifluoromethyl)mercury. However, it appears that the products resulting from the mercury reactions reach an equilibrium which remains unchanged for several days, whereas in the case of the cadmium system, product distribution after several days is often different. This could result from further exchange between the cadmium compounds and the trifluoromethylzinc compounds or slow decomposition of the trifluoromethyl-containing compounds.

The exchange reactions can be represented as shown below to explain the product distribution in the dimethylzinc/bis(trifluoromethyl)mercury and dimethylzinc/bis(trifluoromethyl)cadmium systems.

$$2\,M(CF_3)_2 + Zn(CH_3)_2 \rightleftharpoons 2\,M(CF_3)(CH_3) + Zn(CF_3)_2$$

$$M(CF_3)_2 + 2\,Zn(CH_3)_2 \rightleftharpoons M(CH_3)_2 + 2\,Zn(CF_3)(CH_3)$$

$$3\,M(CF_3)_2 + 2\,Zn(CH_3)_2 \rightleftharpoons 3\,M(CF_3)(CH_3) + Zn(CF_3)(CH_3) + Zn(CF_3)_2$$

(M = Cd, Hg)

TABLE 1

NMR CHEMICAL SHIFTS [a]

	^{19}F	^{1}H
$Zn(CF_3)_2$	38.0	
$Zn(CF_3)(CH_3)$	37.8	−0.32
$Hg(CF_3)(CH_3)$	35.6	0.58
$Hg(CF_3)_2$	33.0	
$Cd(CF_3)(CH_3)$	31.1	−0.16
$Cd(CF_3)_2$	30.4	

[a] Average of values from reactions.

With the above reactions, one could obtain a different ratio of final products by varying the initial concentrations.

With a series of compounds, the ^{19}F chemical shifts are in the following order (toward further deshielding): $Zn(CF_3)_2 > Hg(CF_3)_2 > Cd(CF_3)_2$ and $Zn(CF_3)(CH_3) > Hg(CF_3)(CH_3) > Cd(CF_3)(CH_3)$. The explanation of the ^{19}F chemical shift trend is probably quite complicated since, for a series of methyltrifluoromethyl compounds, the ^{1}H shifts are Zn > Cd > Hg (toward deshielding). Also, the bis(trifluoromethyl) compounds of cadmium and mercury have a lower chemical shift than the respectively methyltrifluoromethyl compound of each metal. On the other hand, bis(trifluoromethyl)zinc has a higher chemical shift than methyl(trifluoromethyl)zinc.

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