Journal of Organometallic Chemistry, 333 (1987) 193–197
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Polar trifluoromethylation reactions. Synthesis and NMR spectra of tris(trifluoromethyl)antimony, $Sb(CF_3)_3$

Dieter Naumann*, **Wieland Tyrra and Ferdinand Leifeld**

Fachbereich Chemie, Universität Dortmund, Postfach 500500, D-4600 Dortmund 50 (F.R.G.)

(Received April 1st, 1987)

Abstract

Bis(trifluoromethyl)cadmium complexes react with antimony trihalides in polar solvents to form $Sb(CF_3)_3$ in high yield. The reactions proceed stepwise and the mono- and bis(trifluoromethyl)antimony compounds formed as intermediates have been identified from their NMR spectra.

Introduction

The first, and until now the only, method for the preparation of $Sb(CF_3)_3$ was that described by Dale et al. in 1957 [1]. $Sb(CF_3)_3$ is the main product from the reaction of elemental antimony with CF_3I at 165–170 °C/50 bar; by-products are $Sb(CF_3)_2I$ and SbI_3. Recently Morrison et al. [2,3], Burton et al. [4] and our group [5] have described the excellent synthetic potential of $Cd(CF_3)_2$ complexes. We showed that these complexes react either as nucleophilic trifluoromethylation reagents or as difluorocarbene reagents [6,7] depending on the reaction conditions. Subsequently we developed a new and convenient method for the high-yield synthesis of $Sb(CF_3)_3$ during our investigations on the polar trifluoromethylation reactions of $Cd(CF_3)_2$ complexes. We describe here the reactions of antimony trihalides with $Cd(CF_3)_2$ complexes, and the NMR spectra of the $SbCF_3$ compounds.

Results

We investigated the reactions of the antimony trihalides SbX_3 (X = Cl, Br, I) with $Cd(CF_3)_2$ complexes in various solvents. The reactions are very slow in diglyme and DMSO, but fast in pyridine, glyme, acetonitrile and DMF. The best solvent is acetonitrile, because there appear to be no side reactions of the $Cd(CF_3)_2$ complexes with the solvent under the conditions used. The rate of reaction of the antimony

0022-328X/87/$03.50

halides SbX_3 decreases in the series X = Cl > Br > I, which corresponds to the order of the extent of dissociation of SbX_3 as indicated by conductivity measurement [8]. (The degree of dissociation corresponding to $2\ SbX_3 \overset{\text{glyme}}{\rightleftarrows} [SbX_2 \cdot 2\text{glyme}]^+ + SbX_4^-$ can also be assessed from molecular weight measurements.) In all cases $Sb(CF_3)_3$ is formed as the final product in high yields:

$$3\ Cd(CF_3)_2 \cdot 2\ CH_3CN + 2\ SbX_3 \rightarrow 3\ CdX_2 + 2\ Sb(CF_3)_3 + 6\ CH_3CN$$

The reaction can be conveniently monitored by ^{19}F NMR spectroscopy. Initial ^{19}F NMR signals grow up at −60.4, −52.3 and −41.2 ppm beside the signals of the $CdCF_3$ compounds (Fig. 1). These new signals came from the mono-, bis- and tris-(trifluoromethyl)antimony compounds. The chemical shifts and coupling constants $J(^{19}F, {}^{13}C)$ do not depend on the halogen in the antimony halide used. At the end of the reaction only the signals of the $CdCF_3$ complexes and $Sb(CF_3)_3$ are observed.

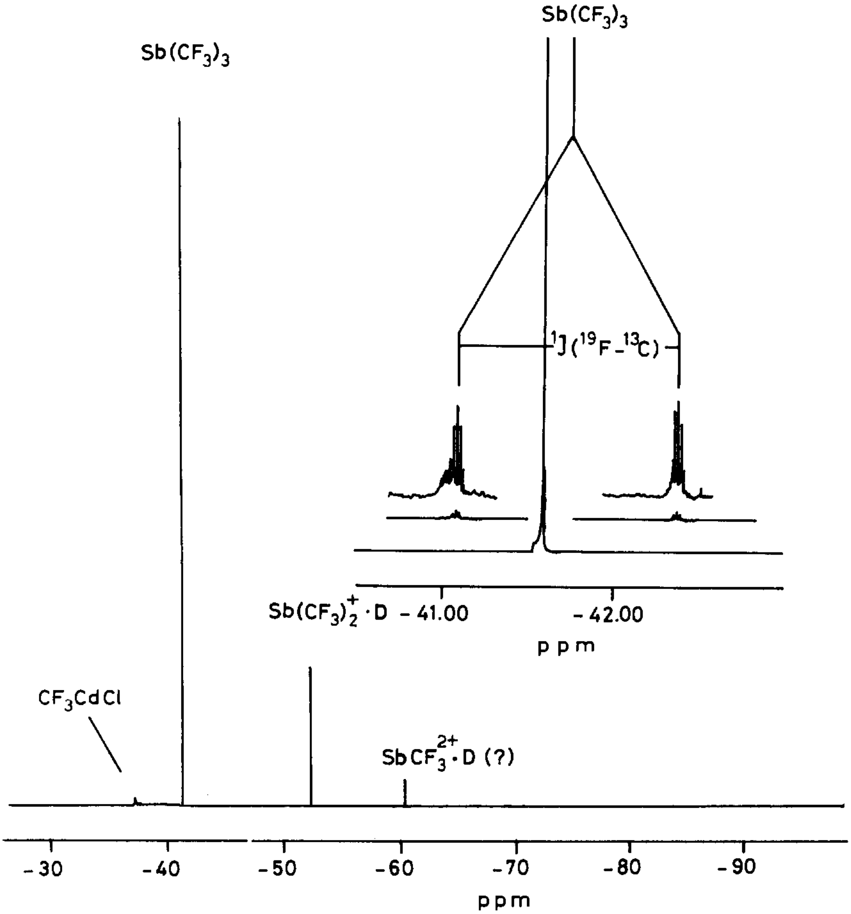

Fig. 1. ^{19} F NMR spectrum of the reaction mixture of $Cd(CF_3)_2{\cdot}2CH_3CN$ and $SbCl_3$ in CH_3CN.

Table 1

^{19}F NMR chemical shifts and coupling constants $^{1}J(^{19}F, ^{13}C)$ and $^{4}J(^{19}F, ^{19}F)$ of the intermediate $Sb(CF_3)_2^+$

SbX_3	$Sb(CF_3)_2^+$			
	δ (ppm)	$^{1}J(^{19}F, ^{13}C)$ (Hz) [a]	$^{4}J(^{19}F, ^{19}F)$ (Hz)	Δδ (Hz)
$SbCl_3$	−52.1	363.2	4.1	38.7
$SbBr_3$	−52.4	363.8	4.1	38.7
SbI_3	−52.4	363.2	4.1	38.7

[a] The ^{13}C satellites are split into quartets.

The intermediately formed mono(trifluoromethyl)antimony compound could not be identified with certainty, because no $^{1}J(F, C)$ coupling could be detected. It is unlikely that $Sb(CF_3)Cl_2$, $Sb(CF_3)Br_2$ and $Sb(CF_3)I_2$ or the conceivable cations $Sb(CF_3)Cl^+$, $Sb(CF_3)Br^+$ and $Sb(CF_3)I^+$ would have identical chemical shifts, because the comparable tellurium compounds show significant shifts to low field in the series $Te(CF_3)_2F_2$ (−53.6 ppm), $Te(CF_3)_2Cl_2$ (−48.9 ppm) and $Te(CF_3)_2Br_2$ (−44.9 ppm) [9]. The formation of a solvated dication $SbCF_3^{2+}$, which is rapidly converted into $Sb(CF_3)_2^+$, is a possibility. $Sb(CF_3)_2^+$ is identified by the splitting into quartets of the ^{13}C satellites in the ^{19}F NMR spectra of the solutions. The chemical shifts and the coupling constants of the $Sb(CF_3)_2^+$ cation do not depend on the halogen of the antimony halide; the data are almost identical (see Table 1).

The final product of all reactions is $Sb(CF_3)_3$, which was also identified from its NMR spectra (Figs. 1 and 2). The ^{19}F NMR spectrum of the acetonitrile solution of

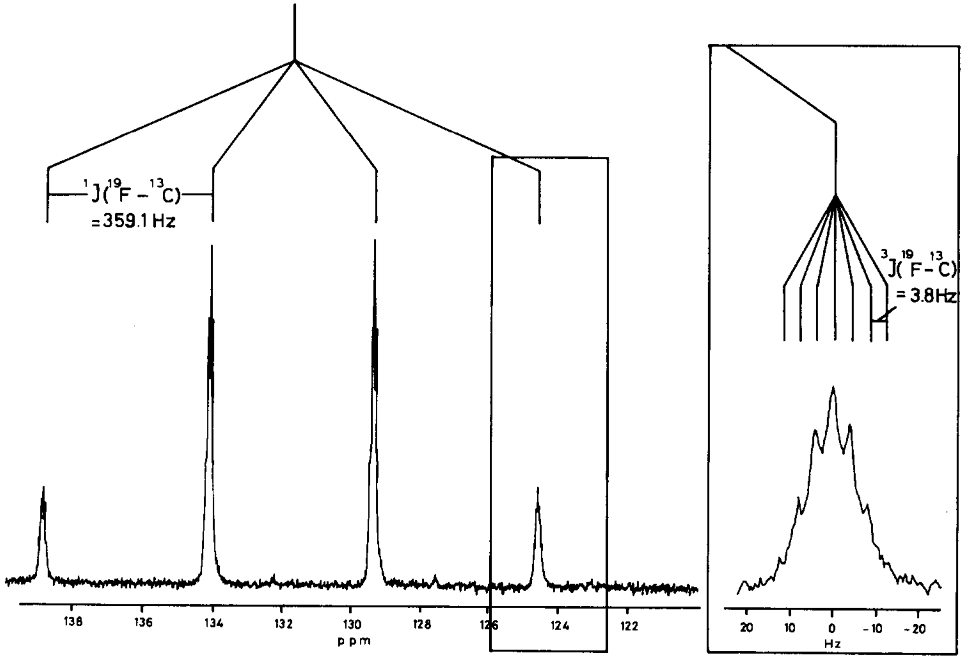

Fig. 2. ^{13}C NMR spectrum of neat $Sb(CF_3)_3$.

$Sb(CF_3)_3$ shows a singlet at -41.2 ppm (neat compound -39.4 ppm [10]). The ^{13}C satellites are split into septets with coupling constants $^1J(^{19}F, ^{13}C)$ 363.2 Hz and $^4J(^{19}F, ^{19}F)$ 4.1 Hz; the isotope shift is about 39 Hz. There is quartet of multiplets at δ 135.9 ppm in the ^{13}C NMR spectrum with $^1J(^{19}F, ^{13}C)$ 363 Hz. The ^{13}C data for the neat compound are: δ (^{13}C) 131.9 ppm, $^1J(^{19}F, ^{13}C)$ 359.1 Hz and $^3J(^{19}F, ^{13}C)$ 3.8 Hz (Fig. 2).

After 8 h reaction at room temperature the ^{19}F NMR spectrum of the solution indicates only the presence of $Cd(CF_3)X$ and $Cd(CF_3)_2$ complexes and $Sb(CF_3)_3$. Tris(trifluoromethyl)antimony is easily isolated in about 80% yield from the reaction mixture by vacuum distillation at $-40\,°C$. From the NMR observations we propose the following reaction steps (donor molecules are omitted):

$$\begin{aligned}
&2\,SbX_3 && \rightleftarrows SbX_2^{+} + SbX_4^{-}\\
&SbX_2^{+} + Cd(CF_3)_2 && \rightarrow Sb(CF_3)X^{+} + Cd(CF_3)X\\
& && \quad\ \downarrow\uparrow\\
& && \{Sb(CF_3)^{2+}\} + X^{-}
\end{aligned}$$

$$\begin{aligned}
&Sb(CF_3)^{2+} + Cd(CF_3)_2 && \rightarrow Sb(CF_3)_2^{+} + Cd(CF_3)^{+} \xrightarrow{X^-} Cd(CF_3)X\\
&Sb(CF_3)_2^{+} + Cd(CF_3)_2 && \rightarrow Sb(CF_3)_3 + Cd(CF_3)^{+} \xrightarrow{X^-} Cd(CF_3)X\\
&Sb(CF_3)_2^{+} + Cd(CF_3)^{+} && \rightarrow Sb(CF_3)_3 + Cd^{2+} \xrightarrow{2X^-} CdX_2\\
&Sb(CF_3)_2^{+} + Cd(CF_3)^{+} + SbX_4^{-} && \rightarrow Sb(CF_3)_3 + CdX^{+} + SbX_3
\end{aligned}$$

If a stoichiometrical excess of antimony trihalide is used, additional equilibria are formed, similar to those described by Emeléus et al. and Walaschewski [11,12] for $As(CF_3)I_2$:

$$\begin{aligned}
&Sb(CF_3)_2^{+} + SbCl_4^{-} && \rightleftarrows Sb(CF_3)_2Cl + SbCl_3\\
&2\,Sb(CF_3)_2Cl && \rightleftarrows Sb(CF_3)_3 + Sb(CF_3)Cl_2\\
&2\,Sb(CF_3)Cl_2 && \rightleftarrows Sb(CF_3)_2Cl + SbCl_3
\end{aligned}$$

When the reaction mixture is stirred at room temperature for 7 d, the ^{19}F NMR spectra indicate the formations of SbF_3 along with some pentafluoroethyl-cadmium and -antimony compounds. These new compounds are formed by partial decomposition of the $SbCF_3$ and $CdCF_3$ derivatives:

$$\begin{aligned}
&Sb(CF_3)_3 && \rightarrow SbF_3 + 3\ |CF_2\\
&Cd(CF_3)_2 && \rightarrow CdF_2 + 2\ |CF_2 \qquad [6]\\
&Sb(CF_3)_3 + n\,|CF_2 && \rightarrow Sb(CF_3)_{3-n}(C_2F_5)_n \quad (n = 1\text{–}3)\\
&Cd(CF_3)_2 + n\,|CF_2 && \rightarrow Cd(CF_3)_{2-n}(C_2F_5)_n \quad (n = 1, 2)
\end{aligned}$$

Experimental

Chemicals. $Cd(CF_3)_2$ complexes were prepared as described previously [13]. The antimony trihalides were dried at $20\,°C/10^{-3}$ Torr for about 12 h ($SbCl_3$: Fa. Merck, Darmstadt; $SbBr_3$ as in ref. 14; SbI_3 as in ref. 15, but in toluene instead of benzene).

Solvents. CH_3CN: Fa. Merck, Darmstadt, dried over P_4O_{10}; glyme: Fa. Aldrich, Beerse, dried over CaH_2; diglyme: Fa. Merck, Darmstadt, dried over $LiAlH_4$; DMF: Fa. Baker, Deventer, dried over CaH_2.

NMR spectra. All spectra were recorded with a Bruker AM 300 FT NMR Spectrometer. ^{19}F NMR: H_0 282.41 MHz; ^{13}C NMR: H_0 75.47 MHz. Standards: CCl_3F (ext., ^{19}F), TMS (ext., ^{13}C).

All reactions were carried out under dry nitrogen. The antimony trihalides are dissolved in 4 ml acetonitrile at $-30\,°C$ and an equimolar amount of solid $Cd(CF_3)_2 \cdot 2CH_3CN$ is added. The reaction mixture is stirred for about 8 h and $Sb(CF_3)_3$ (m.p. $-58\,°C$, b.p. $71.7\,°C$ [1]) then isolated by vacuum distillation at $-40\,°C$.

	$SbCl_3$	$SbBr_3$	SbI_3	
	235	360	501	mg
	1.03	1.01	1.00	mmol
$Cd(CF_3)_2 \cdot 2CH_3CN$	501	501	501	mg
	1.51	1.51	1.51	mmol
Yield of $Sb(CF_3)_3$	269	246	272	mg
	82%	75%	83%	

Mass spectrum of $Sb(CF_3)_3$ (70 eV, $+50\,°C$; only ^{121}Sb containing fragments; m/e). 328 ($Sb(CF_3)_3^+$, 5.6%); 309 ($Sb(CF_3)_2CF_2^+$, 0.9%); 259 ($Sb(CF_3)_2^+$, 29.5%); 209 ($Sb(CF_3)F^+$, 53.3%); 190 ($SbCF_3^+$, 25.5%); 159 (SbF_2^+, 100%); 140 (SbF^+, 31.0%); 121 (Sb^+, 16.8%).

Acknowledgement

We are indebted to the Minister für Wissenschaft und Forschung des Landes Nordrhein-Westfalen and the Fonds der Chemischen Industrie for financial support.

References

1 J.W. Dale, H.J. Emeléus, R.N. Haszeldine and J.H. Moss, J. Chem. Soc., (1957) 3708.
2 L.J. Krause and J.A. Morrison, J. Am. Chem. Soc., 103 (1981) 2995.
3 C.D. Ontiveros and J.A. Morrison, Organometallics, 5 (1986) 1446.
4 D.M. Wiemers and D.J. Burton, J. Am. Chem. Soc., 108 (1986) 832.
5 H. Lange and D. Naumann, J. Fluor. Chem., 27 (1985) 309; D. Naumann and B. Wilkes, J. Fluor. Chem., 27 (1985) 115; W. Dukat and D. Naumann, Rev. Chim. Min., 23 (1986) 589.
6 H. Lange and D. Naumann, J. Fluor. Chem., 27 (1985) 299.
7 G.C. Clark, S.V. Hoskins, T.C. Jones and W.R. Roper, J. Chem. Soc., Chem. Commun., (1983) 719.
8 M. Usanovic and F. Terpugov, Z. Phys. Chem. A, 165 (1933) 39.
9 S. Herberg and D. Naumann, Z. Anorg. Allg. Chem., 494 (1982) 159.
10 J. Apel and J. Grobe, Z. Anorg. Allg. Chem., 453 (1979) 28.
11 H.J. Emeléus, R.N. Haszeldine and E.J. Walaschewski, J. Chem. Soc., (1953) 1552.
12 E.J. Walaschewski, Chem. Ber., 86 (1953) 272.
13 H. Lange and D. Naumann, J. Fluor. Chem., 26 (1984) 1.
14 G. Jander and J. Weis, Z. Elektrochem., 61 (1957) 1275.
15 J.C. Bailar and P.F. Cundy, Inorg. Synth., 1 (1939) 104.