Contribution from the Department of Chemistry,
University of Texas, Austin, Texas 78712

A New Synthesis for (Trifluoromethyl)thio Organometallic Compounds by Low-Temperature Cocondensation of (Trifluoromethyl)thio Radicals and Metal Vapor

Thomas R. Bierschenk and Richard J. Lagow*

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Recently we have reported a new synthesis for σ-bonded metal alkyls which involves a reaction between metal vapor and free radicals generated in a radio-frequency glow discharge:

$$M(g) + nR\cdot \xrightarrow{-196\ °C} M(R)_n \quad R = CH_3, CF_3, SiF_3{}^1$$

The radicals such as methyl, trifluoromethyl, and trifluorosilyl have been found to react with zerovalent metal vapor to produce σ-bonded metal compounds and metal alkyls upon cocondensation with these metals on a −196 °C surface. We have found that many radicals affect this oxidation and in many cases novel organometallic compounds can be formed.

Our most recent work involves the reaction of metal vapor with (trifluoromethyl)thio radicals ($\cdot SCF_3$). The radicals were produced in a low-temperature glow discharge of bis(trifluoromethyl) disulfide. Earlier work using hexafluoroethane, hexafluorodisilane, and ethane has shown that trifluoromethyl, trifluorosilyl, and methyl radicals can be formed in high yield and purity in a glow discharge since the central bond in each of these radical precursors is selectively broken.[1] Bis(trifluoromethyl) disulfide, having a sulfur–sulfur bond (53 kcal/mol) similar in strength to a sulfur–carbon bond (58 kcal/mol), cannot be used as a clean source for $\cdot SCF_3$ radicals.[2] In fact, $\cdot SCF_3$ and $\cdot CF_3$ radicals are both formed in a ratio of approximately 2.7 to 1, which allows one to prepare interesting compounds containing both SCF_3 and CF_3 ligands. Carbon–fluorine bonds are considerably stronger (118 kcal/mol) and are essentially untouched by the plasma.

The first (trifluoromethyl)thio organometallic compound, $Hg(SCF_3)_2$, was first prepared by Brandt, Emeleus and Haszeldine[3] in 1952 by irradiating bis(trifluoromethyl) disulfide in the presence of mercury. A simple, direct, and somewhat surprising route to the mercurial product was reported by Muetterties. The reaction of carbon disulfide with HgF_2 at 250 °C gives $Hg(SCF_3)_2$ in 76% yield.[4] Reaction of $Hg(SCF_3)_2$ with $AgNO_3$ and copper metal at 80 °C produces two new compounds, silver trifluoromethanethiolate ($AgSCF_3$) and copper trifluoromethanethiolate ($CuSCF_3$), respectively.[4] Preparations leading to other metal trifluoromethanethiolates either involve a metathetical reaction between the mercury, silver, or copper trifluoromethanethiolate and the appropriate metal halide[5,6] or involve a thermal cleavage of a (trifluoromethyl)thio derivative in the presence of a metal carbonyl.[7] Typically, CF_3SSCF_3 or CF_3SCl is used. Regardless of the synthetic route used, the reactions invariably involve $\cdot SCF_3$ radicals as intermediates. For instance, the reaction of CF_3SSCF_3 with $Mn_2(CO)_{10}$ at 120 °C gives $[Mn(CO)_4SCF_3]_2$[6] while a similar reaction with Fe_2CO_9 gives $[Fe(CO)_3SCF_3]_2$.[8]

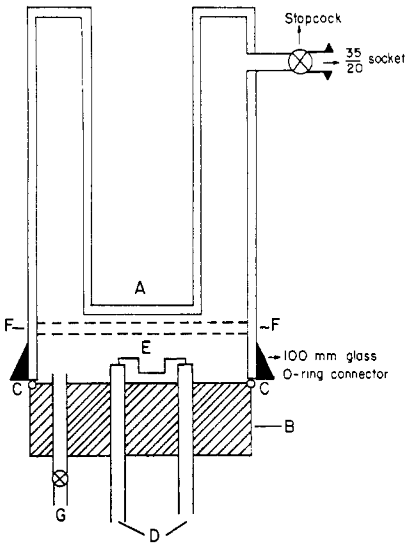

Figure 1.

In addition to the binuclear carbonyl complexes that contain the bridging sulfur groups, several monomeric carbonyl thiolates have been prepared. The photolysis of CF_3SSCF_3 in the presence of the (π-cyclopentadienyl)nickel carbonyl dimer gives rise to $(\pi\text{-}C_5H_5)Ni(CO)SCF_3$.[9] The reaction of $C_7H_8PtCl_2$ with CF_3SAg gives $C_7H_8Pt(SCF_3)_2$ in high yield at room temperature.[6] Recently, Stobart has reported the synthesis of [(trifluoromethyl)thio]germane, $GeH_3(SCF_3)$. The compound was prepared in moderate yields by reacting iodogermane with $AgSCF_3$ at room temperature.[10] We believe that these and other metal SCF_3 compounds will be obtained by the cocondensation of metal atoms and $\cdot SCF_3$ radicals.

Experimental Section

Materials. Tellurium and mercury were obtained from Alfa Inorganics. Bis(trifluoromethyl) disulfide, obtained from PCR, Inc., was further purified by vacuum distillation. The impurities which stopped in a −63 °C trap and passed a −110 °C trap were removed. The tungsten baskets and quartz crucibles were obtained from R. D. Mathis Co.

Analyses and Physical Measurements. Infrared measurements were made with a Beckman IR-20A spectrometer utilizing gas-phase cells with KBr windows. Mass spectra of the gaseous samples were obtained with a Bell and Howell Model 21-490 mass spectrometer. Fluorine NMR spectra were taken on a Varian A56/60 spectrometer operating at 56.47 MHz. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY.

Apparatus. The reactor in which the described syntheses were accomplished is a modification of the one described in a previous publication.[1] The Pyrex cold finger (A) is connected to the reactor base (B) with a glass O-ring connector (C) (see Figure 1). The base was made of brass with water-cooled electrical feed-throughs (D), which were used to resistively heat a crucible heater (E). The radio frequency power was supplied by a Tegal Corp. 100-W, 13.56-MHz radio frequency generator and matching network capacitively coupled to the reactor base and a stainless steel ring (F). The plasma gas, bis(trifluoromethyl) disulfide, enters the reactor through an outlet (G) in the bottom of the base.

General Procedures. A known amount of metal was placed in a crucible, and the reactor was evacuated to approximately 10^{-3} torr. The cold finger was cooled with liquid nitrogen and approximately

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5 g/h of bis(trifluoromethyl) disulfide was delivered to the glow discharge while the metal was vaporized. The desired flow was easily accessible without special metering by allowing the bis(trifluoromethyl) disulfide to slowly vaporize from a chlorobenzene slush (−45 °C). The radio frequency generator power was set at 100 W. After approximately 3 h, the cold finger was allowed to warm and the reaction products were condensed in a −196 °C trap. The products were separated from the unreacted bis(trifluoromethyl) disulfide and plasma gas catenation products by vacuum distillation followed by gas chromatography. The purified product was weighed and a yield, based on the amount of evaporated metal, was calculated.

$Hg(SCF_3)_2$ and $Hg(SCF_3)(CF_3)$. Mercury (1.67 g) was evaporated at a rate sufficient to allow complete evaporation in approximately 3 h. The products were evaporated from the cold finger and vacuum distilled through a −63 °C trap, and the portion retained in the trap was further fractionated by passing through a −15 °C trap. The fraction stopping in the −15 °C trap contained a small amount of the plasma catenation products, 728 mg of $Hg(SCF_3)_2$ (18% yield), 630 mg of $Hg(SCF_3)(CF_3)$ (17% yield), and 51 mg of $Hg(CF_3)_2$ (1.8% yield). The ^{19}F NMR spectra of the $Hg(SCF_3)_2$ product in CH_2Cl_2 gave a singlet at −58 ppm from external CF_3COOH, $J(^{199}Hg-F)$ = 265 Hz, which is in agreement with the values previously reported by Muetterties and co-workers.[4] The second compound, $Hg(SCF_3)(CF_3)$, gave a singlet at −45 ppm from external CF_3COOH for the CF_3 bonded to the mercury, $J(^{199}Hg-F)$ = 1648 Hz. The CF_3 bonded to sulfur gave a singlet at −58 ppm with no observable satellites due to isotope coupling. These findings are consistent with the results reported by Massman and co-workers.[11] The ^{19}F NMR spectrum for $Hg(CF_3)_2$ in methylene chloride gave a singlet at −39.7 ppm from external trifluoroacetic acid with $J(Hg-F)$ = 1295 Hz. The compound appeared identical with $Hg(CF_3)_2$ prepared and purified by other methods.[12,13]

$Te(SCF_3)_2$ and $Te(SCF_3)(CF_3)$. Tellurium (1.34 g) was evaporated over a 3-h period. The products were evaporated from the cold finger and collected in a −196 °C trap. Vacuum distillation of the volatile reaction products through −45, −63, and −95 °C traps resulted in 580 mg of $Te(SCF_3)_2$ (17% yield) being retained in the −45 °C trap while 495 mg of $Te(SCF_3)(CF_3)$ (16% yield) stopped in the −63 °C trap. The unreacted bis(trifluoromethyl) disulfide as well as a yellow impurity passed the −63 °C trap. The ^{19}F NMR spectrum of the impure starting material gave a small singlet at −55.3 ppm from external trifluoroacetic acid with $J(Te-F)$ = 22 Hz. $Te(CF_3)_2$ has a similar color and ^{19}F NMR spectrum and is believed to be the impurity.[12] The concentration of bis(trifluoromethyl)tellurium in the crude CF_3SSCF_3 was estimated to be about 0.30% by gas chromatography. This gives a yield of about 1.5% (40 mg of $Te(CF_3)_2$). $Te(SCF_3)(CF_3)$ was further separated from the plasma catenation products by gas chromatography on a $^3/_8$ in. × 24 ft 10% SE-30 on Chromosorb P column. The $Te(SCF_3)_2$ product was obtained in high purity by condensation on Porapak P contained in a trap on the vacuum line. The contents of this trap were allowed to warm slowly to room temperature, and fractions were collected as they distilled out of the Porapak P. $Te(SCF_3)_2$ was the last fraction to distill off and required overnight pumping and gentle heating (55 °C) to recover all of the material. The product was obtained in greater than 99% purity on the basis of ^{19}F NMR.

$Te(SCF_3)_2$ is a volatile yellow liquid soluble in carbon disulfide.[14] Gas-phase infrared analysis gave bands at 1153 (vs), 1111 (s), 1092 (vs), 752 (m), and 730 (w) cm^{-1}. Mass spectral analysis gave a base peak of *m/e* 69 (CF_3^+ (100%)) and the following comparative abundances of ^{130}Te isotopes (each envelope gave the expected ratio of tellurium and sulfur isotopes): Te^+ (9%), STe^+ (13%), $(SCF_3)Te^+$ (18%), and $(SCF_3)_2Te^+$ (18%). The ^{19}F NMR spectrum gave a singlet at −40.3 ppm from external CF_3COOH with no observable tellurium–fluorine spin–spin coupling.

$Te(SCF_3)(CF_3)$ resembles $Te(SCF_3)_2$ in that it is also a volatile yellow liquid soluble in carbon disulfide. Gas-phase infrared analysis gave bands at 1153 (vs), 1140 (vs), 1098 (s), 1077 (vw), 752 (m), and 728 (m) cm^{-1}. Mass spectral analysis gave a base peak of *m/e* 69 (CF_3^+ (100%)) with the following comparative abundances of Te isotopes: Te^+ (79%), STe^+ (40%), CF_2Te^+ (22%), CF_3Te^+ (81%), $(SCF_3)Te^+$ (74%), and $(CF_3)(SCF_3)Te^+$ (58%). Each of the tellurium-containing fragments occurred in an envelope that had the appropriate distribution of intensities for the isotopes of tellurium and sulfur. The ^{19}F NMR spectrum gave a singlet at −48.5 ppm from external CF_3COOH for the CF_3 bonded to the tellurium, $J(^{125}Te-F)$ = 62 Hz. The CF_3 bonded to sulfur gave a singlet at −38.3 ppm with no observable satellites due to isotope coupling.

Anal. Calcd for $Te(SCF_3)(CF_3)$: S, 10.8; C, 8.1; F, 38.3. Found: S, 11.0; C, 8.3; F, 38.5.

Results and Discussion

The synthesis of (trifluoromethyl)thio organometallic compounds, in spite of the fact that the discharge precursor for this radical is much less specific or selective than in previously reported work, emphasizes one of the strengths of this reaction pathway to σ-bonded organometallic compounds. The advantage is specifically that it is not necessary to have an extremely clean source of radicals in order to affect the reaction. Here the critical factor is simply the statistics of the recombination of metals with radicals. One would expect, and in fact, obtains the statistically expected percentage of the homoleptic compound based on the relative concentrations of each radical present. This is quite in contrast to previous work involving the reaction of radicals with metal halides.[12] This previously reported technique requires extremely clean sources of radicals, for example, the generation of the trifluoromethyl radical from hexafluoroethane, to provide the high yields.

The reaction of (trifluoromethyl)thio radicals generated in a low-temperature glow discharge provides a synthetic route to highly substituted (trifluoromethyl)thio organometallic compounds. In addition to the $\cdot SCF_3$ radical, $\cdot CF_3$ radicals were also produced in a ratio of approximately 2.7 to 1 and resulted in additional products. Reducing the radio frequency power delivered to the plasma had little effect on the ratio of $\cdot SCF_3$ to $\cdot CF_3$ radicals.

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Registry No. $Hg(SCF_3)_2$, 21259-75-6; $Hg(SCF_3)(CF_3)$, 51353-53-8; $Te(SCF_3)_2$, 83665-28-5; $Te(SCF_3)(CF_3)$, 83665-29-6; Hg, 7439-97-6; Te, 13494-80-9; CF_3SSCF_3, 372-64-5.

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[14] $Te(SCF_3)_2$ is thermally unstable. After 2 days at ambient temperature, the compound darkens and new peaks can be seen in the ^{19}F NMR. As a result, we could not obtain acceptable analyses. Anal. Calcd for $Te(SCF_3)_2$: S, 19.4; C, 7.3; F, 34.6. Found: S, 17.8; C, 8.4; F, 36.4.

Contribution from the Department of Chemistry,
University of Iowa, Iowa City, Iowa 52242

Carbon-13 NMR Spectroscopy of High-Spin Iron(II) Porphyrin Complexes

Ataollah Shirazi, Eric Leum, and Harold M. Goff*

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A combination of short electronic relaxation times and large zero-field splittings for paramagnetic iron(II) porphyrin species precludes direct ESR measurements but results in sharp, well-resolved NMR spectra. Accordingly, proton NMR studies have previously been used to elucidate the electronic structure, magnetic anisotropy, ligand binding, and aggregation properties of intermediate-spin (S = 1) square-planar[1-5] and

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