The Second Dimension in Metal Vapor Chemistry. A New General Synthesis for Metal Alkyls

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Abstract: A new synthesis has been developed for preparation of $M(R)_n$ metal alkyls and other similar compounds. The reactive free radicals $CH_3\cdot$, $CF_3\cdot$, and $SiF_3\cdot$ have been cocondensed with metals on a cold finger at −196 °C and oxidize the metals to the compounds $Hg(CF_3)_2$, $Te(CF_3)_2$, $Te_2(CF_3)_2$, $Bi(CF_3)_3$, $Hg(CH_3)_2$, $Cd(CH_3)_2$, $Bi(CH_3)_3$, $Sn(CH_3)_4)$, $Ge(CH_3)_4$, and $Hg(SiF_3)_2$.

In the field of metal vapor chemistry, since its inception marked by the initial papers of Timms[1] and Skell,[2a] the major thrust has been syntheses involving cocondensation of π-bonding ligands with metal vapor with the most notable exceptions being use of metal atoms as dehalogenation agents or in Grignard-like reactions.[2b,c] Most of the products formed are ones in which the metal atom is in a low valence state π bonded or complexed to various ligands. Such reactions have constituted an important major research effort in inorganic chemistry over the past 10 years:[3]

$$M(g) + nL \xrightarrow[-196\ ^\circ C]{} ML_n$$

We have found, and report the initial experiments in this paper, a new synthesis for σ-bonded metal alkyls and similar compounds involving a reaction between metal vapor and free radicals generated in a radio frequency glow discharge:

$$M(g) + nR\cdot \xrightarrow[-196\ ^\circ C]{} MR_n \text{ where } R = CH_3, CF_3, SiF_3$$

The radicals such as methyl, trifluoromethyl, and trifluorosilyl radicals used in this work have been found to oxidize zerovalent metals to their highest oxidation state upon cocondensation with these metals on a cold surface at −196 °C.

We have determined that a number of sources of radicals can be used for this technique; however, the low-temperature glow discharge is a very convenient source of radicals for synthetic work. It has been employed previously in our laboratory to generate trifluoromethyl radicals from hexafluoroethane without producing significant amounts of other reactive species:[4]

$$C_2F_6 \xrightarrow{\text{r.f.}} 2CF_3\cdot$$

$$nCF_3\cdot + MX_n \rightarrow M(CF_3)_n + n/2X_2 \text{ where } X = I, Br, Cl$$

Reactions of this type, although totally different in principle from those reported here, have expanded the extent of trifluoromethyl organometallic chemistry significantly.[5]

With the newer technique it is also possible to use other symmetrical molecules with a relatively weak central bond, such as ethane to produce methyl radicals and Si_2F_6 to produce trifluorosilyl radicals. The carbon–carbon bond in ethane has a bond strength of approximately 86 kcal/mol and the carbon–hydrogen bond strength is 104 kcal/mol.[6] Although this difference in bond strengths of about 15 kcal/mol is substantially smaller than is the case with hexafluoroethane, where it is at least 40 kcal/mol, no substantial quantities (none were observed in NMR spectra) of the metal alkyls produced by the reaction of metal atoms with an ethane discharge contained ethyl groups.

Experimental Section

Materials, Analyses, and Physical Measurements. The metals and antimony halides used as starting materials were obtained from Alfa Inorganics. The hexafluoroethane was dielectric grade Du Pont Freon 116.5. The ethane was "chemically pure grade" from Big Three Industries Inc., degassed before using. Hexachlorodisilane was obtained from Polysciences Inc. Elemental analyses were performed by Schwarzkopf Laboratories, Woodside, N.Y. Infrared spectra were obtained with a Beckman IR-20A spectrometer utilizing KBr disk samples or gas-phase cells with KBr windows. Fluorine and hydrogen NMR spectra were taken on a Varian A 56/60 spectrometer operating at 56.47 and 60 MHz, respectively. Mass spectra were obtained with a Bell and Howell Model 21-491 mass spectrometer.

Apparatus. The reactor in which the syntheses were accomplished is shown in Figure 1. The cold finger (A) and the reactor are connected with a glass O-ring connector (B). The base (C) was made of brass with water-cooled electrical feedthroughs (D) for the tungsten basket or crucible heater (E). The base and reactor were connected with an O-ring junction (F). The Pyrex reactor consisted of two halves separated by an O-ring (G). 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 by two metal rings (H and I). The plasma gas (i.e., hexafluoroethane) comes in at the outer jacket of the reactor (J) into a ballast volume and goes through a slit approximately 0.5 in. wide in the inner tubing and between the metal rings (H and I). The tungsten basket or crucible heater were resistively heated by passing current through them. Metals more volatile than bismuth were evaporated from a quartz crucible heated by tungsten wire around the outside of the crucible. Bismuth and less volatile metals were placed in a wound tungsten wire basket which was coated with aluminum oxide cement. The tungsten baskets, crucibles, and crucible heaters were obtained from R. D. Mathis Co.

General Procedure. With the crucible or tungsten basket filled with a known amount of metal, the reactor was assembled and evacuated. The cold finger was cooled with liquid nitrogen. The gaseous radical precursor (C_2F_6, C_2H_6, Si_2F_6) was added at a rate between 1 and 2 mmol/min. The radio frequency generator power was set at 100 W and the metal was evaporated. When the reaction was completed, the cold finger was warmed and the excess plasma gas removed by vacuum distillation. The remaining mixture of product and plasma gas catenation products was separated to give a pure compound. The product was then weighed and a yield based on the amount of metal evaporated was calculated.

Reactions of Metals with Trifluoromethyl Radicals. Synthesis of $Hg(CF_3)_2$. Mercury (3.2 g) was evaporated at a rate just below the rate required to turn the color of the cold finger black with unreacted mercury. All of the mercury evaporated in slightly under 3 h. The products were evaporated from cold finger and vacuum distilled through a −78 °C trap and the portion retained in the trap was vacuum sublimed onto an ice-cooled cold finger. Material (4.77 g, 89% yield) scraped from the cold finger was identified as $Hg(CF_3)_2$ by NMR analysis in CH_2Cl_2 solution. The NMR gave a singlet at −39.7 ppm from external CF_3COOH with $J(^{199}Hg\text{–}F) = 1294$ Hz.

Synthesis of $Te(CF_3)_2$ and $Te_2(CF_3)_2$. Te (1.5 g) was evaporated over about a 3-h period. The products were evaporated from the cold finger and collected in a −131 °C trap. Vacuum distillation at −95 °C gave

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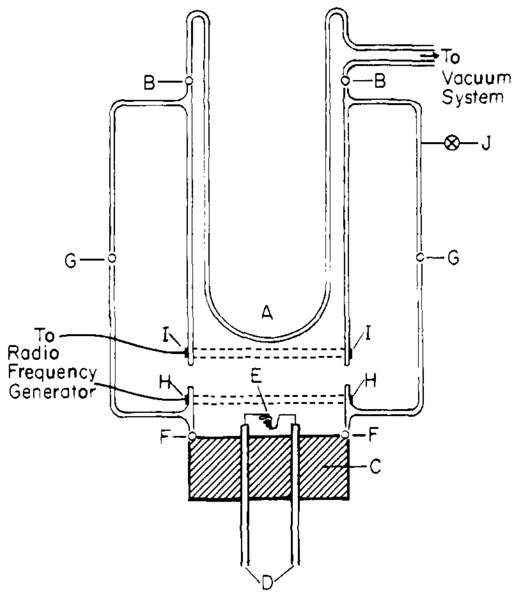

Figure 1.

$Te(CF_3)_2$ with a small amount of fluorocarbon products that could be removed as in ref 4 to give 310 mg of $Te(CF_3)_2$ (10% yield). ^{19}F NMR gave a singlet at −55.3 ppm from external CF_3COOH, $J(^{125}Te-F) = 22$ Hz. The IR spectrum was identical with that reported earlier.[4] Vacuum distillation at −45 °C gave $(CF_3)_2Te_2$ about 90% pure. Further purification as shown in ref 4 gave 480 mg of $Te_2(CF_3)_2$. ^{19}F NMR gave a singlet at −51.0 ppm from external CF_3COOH with $J(^{125}Te-F) = 93$ Hz. The infrared spectrum agreed with that previously reported.[4]

Synthesis of $Bi(CF_3)_3$. Bismuth (1.5 g) was evaporated over a 3-h period and the products from the cold finger were vacuum distilled through a −78 °C trap. This material was then separated from fluorocarbons produced in the plasma by gas chromatography on a SE-30 on Chromosorb P column to give 920 mg of $Bi(CF_3)_3$ (31% yield). Fluorine NMR showed a singlet at −44 ppm from external CF_3COOH. The infrared spectrum was in good agreement with that previously reported.[7]

Synthesis of $Sn(CF_3)_4$. Tin (1.5 g) was evaporated over a 3-h period and the volatile products from the cold finger were collected in a −95 °C trap. This material was then separated from fluorocarbons by gas chromatography on a SE-30 on Chromosorb P column to give 38 mg of $Sn(CF_3)_4$ (0.8% yield). ^{19}F NMR in CH_2Cl_2 solution showed a singlet at −37 ppm from external CF_3COOH with $J(117/119) = 499/526$ Hz.

Reactions of Metals with Methyl Radicals. All methyl compounds were separated by gas chromatography on a ⅜ in. × 25 ft 10% SE-30 on Chromosorb P column. Although no spectral data are given, identities of all compounds were confirmed by comparing the spectra of the compounds with ones made by standard literature methods or obtained from Alfa Inorganics.

Synthesis of $Hg(CH_3)_2$. Approximately 1.5 g of mercury was evaporated over a 3-h period in an ethane discharge. The volatile products were collected in a −95 °C trap. $Hg(CH_3)_2$ (160 mg, 9% yield) was obtained after separation on a gas chromatograph.

Synthesis of $Cd(CH_3)_2$. Cadmium (1.5 g) was vaporized in an ethane discharge in about a 3-h period. The volatile products were collected in a −78 °C trap, purified by gas chromatography, and weighed to give 580 mg (31% yield) of $Cd(CH_3)_2$.

Synthesis of $Bi(CH_3)_3$. Bismuth (1.2 g) was evaporated in about 2 h in an ethane discharge. The volatile products were collected in a −78 °C trap, purified by gas chromatography, and weighed to give 195 mg of $Bi(CH_3)_3$ (13% yield).

Synthesis of $Sn(CH_3)_4$. Tin (1.4 g) was evaporated over a 3-h period in an ethane plasma. The volatile products were collected in a −95 °C trap. After purification, 175 mg of $Sn(CH_3)_4$ was obtained (9% yield).

Synthesis of $Ge(CH_3)_4$. Germanium (0.9 g) was evaporated in about 2 h in an ethane discharge. The products were collected in a −119 °C trap. The weight of $Ge(CH_3)_4$ after separation was 265 mg (16% yield).

Reaction of Metal with SiF_3 Radicals. Synthesis of $Hg(SiF_3)_2$. Freshly sublimed antimony trifluoride (30 g, 0.168 mol) was placed in a stopcocked 2-L round-bottom flask and evacuated. Approximately 1 mL of antimony pentachloride catalyst and 11 mL (0.65 mol) of hexachlorodisilane were condensed in the flask, which was then closed and placed in a 60 °C oven for about 16 h. The products were vacuum distilled (hexafluorodisilane passes −78 °C and stops in a −131 °C slush) to yield approximately 10 g (0.6 mol) of hexafluorodisilane.

Mercury (1.5 g) was evaporated over a 3-h period in a hexafluorodisilane discharge. The volatile products from the cold finger were then pumped through an ice-salt cooled trap and the solids were scraped out of the reactor and ice-salt cooled trap in an inert atmosphere. The volatile products could then be vacuum distilled to recover over 95% of the hexafluorodisilane, which could be reused. The volatiles of bis(trifluorosilyl)mercury and mercury metal were too similar to be effectively separated by sublimation. The solids were removed and mixed with a slight excess of sulfur. This mixture was then sublimed, extracted with carbon disulfide to remove the sulfur, and sublimed again to give 730 mg of $Hg(SiF_3)_2$ (26% yield). $Hg(SiF_3)_2$ is a white, crystalline solid which is insoluble in all organic or inorganic solvents tried. Infrared analysis of a KBr disk sample gave bands at 880 (vs), 825 (s), 800 (vs), 445 (s), and 305 cm^{-1} (w). Mass spectral analysis gave a base peak of *m/e* 85 (SiF_3^+) (100%) and the following comparative abundances of ^{198}Hg isotopes (each envelope possessed the expected peak ratios for mercury and silicon isotopes): Hg^+ (21%), SiF_2Hg^+ (1.9%), SiF_3Hg^+ (14%), $Si_2F_5Hg^+$ (0.4%), and $Si_2F_6Hg^+$ (0.8%). Reaction of $Hg(SiF_3)_2$ with elemental fluorine in a passivated Kel-F and stainless steel system gave SiF_4. $Hg(SiF_3)_2$ is easily hydrolyzed but can be kept for long periods of time in an inert atmosphere. Anal. Calcd for $Hg(SiF_3)_2$: Hg, 54.1; Si, 15.15; F, 30.75. Found: Hg, 52.1; Si, 13.9; F, 29.4.

Results and Discussion

The oxidation of the metal vapors by the plasma-produced radicals appears to occur in both the gas and condensed phases. If the reaction is run without the cold finger, some compound can usually be made but in dramatically smaller yields. Unlike the reactions of Skell and Girard[8] and others, the reaction appears to occur as the reagents condense and no changes are seen on warmup. It should be possible therefore to look for metal–ligand σ bonds in the matrix for virtually any ligand which can be produced as a radical.

Specifically, in this work, radicals have been generated from hexafluoroethane, ethane, and hexafluorodisilane:

$$C_2F_6 \xrightarrow{\text{r.f.}} 2CF_3\cdot$$

$$C_2H_6 \xrightarrow{\text{r.f.}} 2CH_3\cdot$$

$$Si_2F_6 \xrightarrow{\text{r.f.}} 2SiF_3\cdot$$

It should be very clear that the oxidation of metal atoms to their most stable (and usually highest) oxidation state by radicals on a cold surface or in the gas phase should be possible for radicals of almost any type. While one might have predicted that highly electronegative radicals such as CF_3 and SF_5 would accomplish this oxidation, the fact that it occurs in such a facile manner for the methyl radical, which has no particularly great oxidizing power, is a very encouraging sign. Certainly, new organometallic compounds from ethyl radicals, phenyl radicals, and other organic radicals of most types are plausible. The fact that the reaction appears to occur primarily on the cold finger of the reactor or in the very short time period preceding condensation offers the possibility that very unstable compounds (i.e., compounds that decompose at −50 °C) might be isolated by extracting the matrix with a cold solvent or by adding other stabilizing ligands, as has become common practice in the previous metal vapor–ligand reactions. There is a distinct possibility that our work on cocondensation of transition-metal vapors and methyl radicals which is currently in progress could establish the existence of methyl transition metal alkyl species too unstable to be prepared by the conventional routes which often require much higher activation energy.

The use of a radio frequency glow discharge as a radical source has the advantage of having few competitive reactive species produced when a symmetric molecule with a relatively weak central bond is used. A disadvantage of this method is that there must be a pressure of about 10^{-2} Torr for the plasma to be sustained. Products must also be separated from unreacted plasma gas and the small amount of catenation products produced by the plasma. However, it is a very convenient source of radicals for synthetic work.

The synthesis of transition metal alkyl compounds is difficult owing to the problem in vaporizing quantities of metal at 10^{-2} Torr. But such problems have, for the most part, been overcome and a discussion of these reactions will appear in the near future.[9]

It is clear from these results that the consequences of this new method are far reaching:

(1) Currently, work is underway on the generation of σ-bonded BF_2 metallic compounds using B_2F_4 as a source of BF_2 radicals and with SF_5 radicals generated from S_2F_{10} directed toward the preparation of σ-bonded $M(SF_5)_n$. Also, $PF_2\cdot$ reactions, $SiCl_3\cdot$ reactions, and $SiH_3\cdot$ reactions are under investigation. Other studies are planned with such radicals as $\cdot OCF_3$, $\cdot SCF_3$, $\cdot OCH_3$, $\cdot SCH_3$, $\cdot NH_2$, $\cdot NF_2$, and $\cdot PH_2$.

(2) Further, it is clear that the oxidation of many species other than pure metals is possible on cold surfaces with radicals. In particular, metal halides, such as $SnCl_2$, are converted primarily to $Sn(CF_3)_2Cl_2$.[10] Other metal subfluorides or metal oxides which are either stable at ambient temperatures or generated solely as high-temperature species are also oxidized. A possible criterion for oxidation here is simply that the ionization potentials of the metal or nonmetal compounds must be comparable to those of the corresponding main-group or transition metals so that oxidation may take place.

(3) A further ramification of the present work is the possibility of cocondensing metals and radicals in argon and other types of matrices for spectroscopic study. It would appear that one could use an apparatus as simple as a diathermy plasma source and metal atoms to prepare by cocondensation many new species in matrices. Of particular interest should be the cocondensation of transition metals with such species as methyl radicals to produce unsaturated (i.e., lower valence than normal) $M(R)_{n-1}$, $M(R)_{n-2}$, etc., where the metal is not coordinatively saturated. The structures of such species would be of unusual interest in view of the fact that unsaturated metal alkyls have been proposed by many workers to be active species in homogeneous catalysis. Such spectroscopic work on unsaturated metal carbonyls ($M(CO)_{n-1}$, $M(CO)_{n-2}$) had been studied previously by Turner, Ozin, and others.[11]

Many new compounds will certainly result from applications of this technique. It should be noted that, while P–SiF_3 compounds have been prepared by new techniques,[12] the compound $Hg(SiF_3)_2$ is the first example of a trifluorosilyl metallic compound.

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