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A NEW SYNTHESIS FOR METHYL/TRIFLUOROMETHYL ORGANOMETALLIC COMPOUNDS BY LOW TEMPERATURE COCONDENSATION OF TRIFLUOROMETHYL RADICALS AND MAIN GROUP METHYL ALKYLS

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Summary

The reaction of trifluoromethyl radicals produced in a radio frequency discharge of hexafluoroethane with trimethylphosphine, tetramethyltin, dimethylmercury, trimethylbismuth and tetramethyllead gave complexes with methyl and trifluoromethyl substituents. The compounds dimethyl(trifluoromethyl)phosphine, trimethyl(trifluoromethyl)tin, methyl(trifluoromethyl)mercury, bis(trifluoromethyl)mercury, dimethyl(trifluoromethyl)bismuth, bis(trifluoromethyl)methylbismuth, trimethyl(trifluoromethyl)lead and bis(trifluoromethyl)dimethyllead were isolated along with the new compound, tris(trifluoromethyl)methyllead. The synthesis and physical properties of the compounds are reported.

Introduction

Over the past several years, we have developed in our laboratory at least four different synthetic techniques which have been useful in preparing new trifluoromethyl organometallic compounds in good yields [1–4]. The novel synthetic method presented here offers the advantage of using convenient starting materials. The major disadvantage of this technique is that under the conditions studied the yields tend to be lower than the methods previously developed in our laboratory. Nevertheless, with this method it is possible to prepare several new compounds.

Recently we reported a new synthetic technique for preparing organometallic compounds containing σ-bonded alkyl ligands [4]. This reaction involved the codeposition of metal vapors on a liquid-nitrogen cooled surface with alkyl radicals which were generated in a low temperature glow discharge. For example, we reported that a wide variety of metal vapors would react with methyl, trifluoromethyl, trifluorosilyl and trifluoromethylthio radicals to give the corresponding completely substituted metal alkyl complexes. These radicals were easily generated in a low temperature glow discharge of ethane, hexafluoroethane, hexafluorodisilane

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and bis(trifluoromethyl) disulfide. In fact, practically any symmetrical molecule having a central bond which is at least 20 to 30 kcal/mol weaker than the other bonds in the molecule can be used to cleanly generate radicals in a low power plasma (30 to 75 W).

Work is currently underway in our laboratories to expand the list of radicals which can be used successfully to prepare metal complexes in this manner. Preliminary results suggest that SiH_3, PF_2 and NF_2 radicals will combine with selected metals to give stable complexes [5]. Additionally, we have demonstrated that organometallic complexes containing two or more different ligands can be prepared by vaporizing metals in the presence of a plasma comprised of two or more gases. For instance, a mixture of ethane and hexafluoroethane gave both methvl and trifluoromethyl radicals, which when condensed with metal vapors on a liquid nitrogen cooled surface produced organometallic complexes containing both methyl and trifluoromethyl ligands.

Several mixed methyl and trifluoromethyl compounds are known and were prepared using more conventional solution techniques. The reaction of trifluoroiodomethane with a number of Main Group metal alkyl compounds gave products containing both methyl and trifluoromethyl ligands [6]. An analogous reaction using methyl iodide and trifluoromethylmetal complexes also has some precedence [7]. Alternatively, bis(trifluoromethyl)mercury will react with some methyl substituted metal complexes to give products containing the two ligands [8]. In each case, the reactions are extremely limited and give the desired products in only isolated circumstances. For this reason, a more general reaction, such as the plasma reaction described in this paper, was needed in order that a wide variety of products could be systematically prepared.

Experimental

Materials, analysis and physical measurements

The hexafluoroethane was dielectric grade DuPont Freon 116. Dimethylmercury, lead iodide, tin(IV) bromide, bismuth triiodide and triphenylphosphite were purchased from Alfa Inorganics. Tetramethyllead, tetramethyltin, trimethylbismuth and trimethylphosphine were prepared from the reaction of the methyl-Grignard reagent and the corresponding Main Group halide. Gas chromatography was carried out on a Bendix 2300 gas chromatograph equipped with an automatic temperature programmer. The infrared spectra were obtained with a Beckman IR-20A spectrometer. Hydrogen and fluorine NMR spectra were recorded on a Varian EM 390 spectrometer operating at 90 and 84.6 MHz, respectively. Mass spectra were obtained from a Bell and Howell model 21-490 mass spectrometer operating at 70 eV with a source temperature of 240°C.

Apparatus

The Pyrex reactor used is shown in Fig. 1. The top portion of the reactor has a 40 mm cold finger (A) that was sealed to the reactor bottom by a 75 mm O-ring connector (B). The metal alkyl and hexafluoroethane were metered into 10 mm glass tubing (C and D) and allowed to mix before they entered the inlet (E). A Tegal Corp., 100 W, 13.56 MHz radio frequency generator equipped with a matching

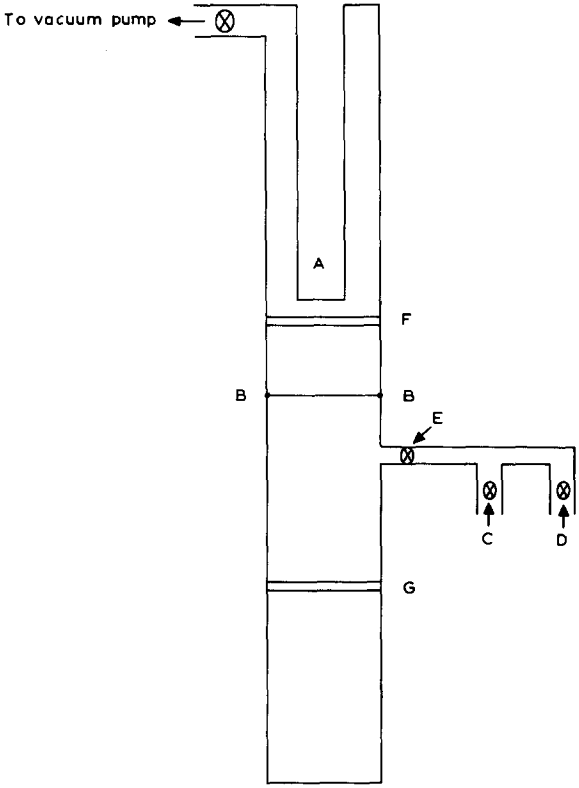

Fig. 1. Pyrex reactor used in the experiments.

network was used to generate the radio frequency power. The discharge was produced by capacitively coupling the two metal bands (F and G).

General procedure

The Main Group metal alkyl was preweighed and the reactor was assembled and evacuated overnight. The cold finger was filled with liquid nitrogen and the mixture of hexafluoroethane and alkylmetal was introduced at an average ratio of 25/1 with the radio frequency power turned on. After approximately 2 h, the reaction was terminated and the excess hexafluoroethane was vacuum distilled through a − 100°C slush. The mixture of products and plasma gas catenation products which condensed in the − 100°C trap were further separated on a 3/8″ gas chromatography column packed with 10% SE-30 on Chromosorb P. The separated compounds were then weighed and a yield was calculated based on the amount of metal alkyl vaporized. The ^1H and ^{19}F NMR were taken as dilute solutions of each compound. After obtaining the NMR spectra, the mass spectrum was obtained for each compound.

Results and discussion

The amount of metal alkyl vaporized, along with the yields for the corresponding methyl/trifluoromethyl substituted compounds are given in Table 1. ^1H and ^{19}F

TABLE 1

YIELDS FOR METHYL/TRIFLUOROMETHYL ORGANOMETALLIC COMPOUNDS

Initial compounds	Vaporized (mg)	Isolated compounds	Yields (mg (%))
P(CH$_3$)$_3$	573.1	P(CH$_3$)$_2$CF$_3$	33.9(3.5)
Sn(CH$_3$)$_4$	305.0	Sn(CH$_3$)$_3$CF$_3$	12.2(3.1)
Hg(CH$_3$)$_2$	224.2	Hg(CH$_3$)CF$_3$	9.3(3.4)
		Hg(CF$_3$)$_2$	15.9(4.9)
Bi(CH$_3$)$_3$	369.7	Bi(CH$_3$)$_2$CF$_3$	29.0(5.1)
		BiCH$_3$(CF$_3$)$_2$	4.0(0.9)
Pb(CH$_3$)$_4$	1149.2	Pb(CH$_3$)$_3$CF$_3$	24.5(1.9)
		Pb(CH$_3$)$_2$(CF$_3$)$_2$	5.8(0.4)
		PhCH$_3$(CF$_3$)$_3$	2.4(0.2)

NMR data for the substituted compounds can be found in Table 2. The mass spectral results are given in Table 3.

The ^{1}H and ^{19}F NMR spectra obtained for the methyl/trifluoromethyl metal complexes were in good agreement with the literature values [9–14]. In the mass spectrum the expected isotopic patterns were observed for each fragment and the parent ion was observed for all but one compound. An IR spectrum for tris(trifluoromethyl)methyllead in a 10 cm gas cell equipped with KBr windows gave bands at 2960m, 1370s, 1300vs, 1180vs, 1105vs, 1070vs, 900m, 705m and 695m cm^{-1}.

A more general synthesis of Main Group complexes with methyl and trifluoromethyl groups has been found. A glow discharge of hexafluoroethane with Main Group methyl complexes produced mixed methyl and trifluoromethyl Main Group complexes. The amount of trifluoromethyl substitution is dependent on the bond strength of the Main Group methyl complex used. The carbon and Main Group element bond follows a decreasing bond strength of P > Sn > Hg > Bi > Pb [15].

TABLE 2

^{1}H AND ^{19}F NMR DATA OF METHYL/TRIFLUOROMETHYL ORGANOMETALLIC COMPOUNDS[a,b]

Compound	CH$_3$[c]	^2J(MH)[d,e]	CF$_3$[c]	^2J(MF)[d,e]
P(CH$_3$)$_2$CF$_3$	1.30	3.3	−12	66
Sn(CH$_3$)$_3$CF$_3$	0.42	64.2/60.0	−28	288/274
Bi(CH$_3$)$_2$CF$_3$	1.40	–	−37	–
BiCH$_3$(CF$_3$)$_2$	1.46	–	−41	–
HgCH$_3$(CF$_3$)	1.20	138.0	−36	981
Hg(CF$_3$)$_2$	–	–	−38	1297
Pb(CH$_3$)$_3$CF$_3$	1.10	72.0	−33	263
Pb(CH$_3$)$_2$(CF$_3$)$_2$	1.50	88.5	−37	403
PbCH$_3$(CF$_3$)$_3$	2.00	94.0	−40	601

[a] ^{1}H NMR were taken on a dilute solution of CCl$_4$ and referenced to external TMS. ^{19}F NMR were taken on a dilute solution of diethyl ether and referenced to external TFA. [b] Singlets were observed in all cases except for the phosphorus compound, which gave a doublet. [c] Chemical shifts given in ppm (negative values are deshielded). [d] Coupling constants given in Hz. [e] M = P, $^{117/119}$Sn, Bi, ^{199}Hg and ^{207}Pb.

TABLE 3

MASS SPECTRA OF METHYL/TRIFLUOROMETHYL ORGANOMETALLIC COMPOUNDS[a]

Compound	Fragments[b]
$P(CH_3)_2CF_3$	130, $CF_3P(CH_3)_2^+$ (67%); 80, $FP(CH_3)_2^+$ (39%); 69, CF_3^+ (50%); 65, $FPCH_3^+$ (48%); 61, $P(CH_3)_2^+$ (100%); 31, P^+ (6%)
$Sn(CH_3)_3CF_3$	217, $CF_3Sn(CH_3)_2^+$ (28%); 167, $FSn(CH_3)_2^+$ (40%); 163, $Sn(CH_3)_3^+$ (100%); 133, $SnCH_3^+$ (62%); 118, Sn^+ (48%); 69, CF_3^+ (60%)
$Bi(CH_3)_2CF_3$	308, $CF_3Bi(CH_3)_2^+$ (68%); 293, $CF_3BiCH_3^+$ (67%); 243, $FBiCH_3^+$ (84%); 239, $Bi(CH_3)_2^+$ (100%); 224, $BiCH_3^+$ (86%); 209, Bi^+ (97%); 69, CF_3^+ (42%)
$BiCH_3(CF_3)_2$	362, $(CF_3)_2BiCH_3^+$ (2%); 343, $CF_3CF_2BiCH_3^+$ (15%); 293, $CF_3BiCH_3^+$ (32%); 243, $FBiCH_3^+$ (24%); 224, $BiCH_3^+$ (19%); 209, Bi^+ (75%); 69, CF_3^+ (100%)
$HgCH_3(CF_3)$	286, $CF_3HgCH_3^+$ (2%); 271, CF_3Hg^+ (4%); 267, $CF_2HgCH_3^+$ (64%); 202, Hg^+ (25%); 69, CF_3^+ (100%)
$Hg(CF_3)_2$	340, $CF_3HgCF_3^+$ (2%); 321, $CF_2HgCF_3^+$ (13%); 271, $HgCF_3^+$ (50%); 202, Hg^+ (47%); 69, CF_3^+ (100%)
$Pb(CH_3)_3CF_3$	322, $CF_3Pb(CH_3)_3^+$ (12.5%); 307, $CF_3Pb(CH_3)_2^+$ (10%); 253, $Pb(CH_3)_3^+$ (63%); 223, $PbCH_3^+$ (75%); 208, Pb^+ (100%); 69, CF_3^+ (25%)
$Pb(CH_3)_2(CF_3)_2$	357, $CF_3(CF_2)Pb(CH_3)_2^+$ (4%); 269, $CFPb(CH_3)_2^+$ (15%); 254, $CFPbCH_3^+$ (100%); 239, $CFPb^+$ (31%); 223, $PbCH_3^+$ (98%); 208, Pb^+ (96%); 69, CF_3^+ (100%)
$PbCH_3(CF_3)_3$	361, $(CF_3)_2PbCH_3^+$ (33%); 254, $CFPbCH_3^+$ (100%); 242, $FPbCH_3^+$ (69%); 208, Pb^+ (26%); 69, CF_3^+ (98%)

[a] Mass spectra were obtained on gaseous samples with the exception of $Hg(CF_3)_2$ which was a solid sample. [b] *m/e*, fragment (percentage relative to base peak).

Only a single trifluoromethyl group was exchanged for trimethylphosphine and tetramethyltin to give dimethyl(trifluoromethyl)phosphine and trimethyl(trifluoromethyl)tin. The weaker bonded methyl complexes of mercury, bismuth and lead exchanged more than one trifluoromethyl group.

The organometallic compounds produced with methyl and trifluoromethyl substitution can decompose in a glow discharge. The major products formed are methyl metal fluorides. The low yields obtained for the main group complexes with both methyl and trifluoromethyl groups could be explained by the elimination of difluorocarbene or carbene in cases where methyl alkyls are photochemically unstable.

The reaction of trifluoromethyl radicals generated in a low temperature glow discharge provides an alternate synthetic route to trifluoromethyl-substituted organometallic compounds. The volatile properties of Main Group methyl complexes eliminates the high temperature equipment needed for conventional reactions with trifluoromethyl radicals to produce trifluoromethyl-substituted organometallic compounds. Similarly, transition metal complexes which are volatile compounds can be used for the synthesis of trifluoromethyl-containing compounds.

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