Preparation and Properties of Trifluoromethylated Aryl Derivatives of Germanium, Tin, and Lead. High-Yield Syntheses of Trifluoromethylbenzene

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Received January 10, 2000

Ligand exchange reactions of $Cd(CF_3)_2$·glyme with a number of aryl-containing Pb, Sn, and Ge halides, acetates, and thioethers were examined in THF or $CHCl_3$. With an excess of trifluoromethylating agent and relatively lengthy reaction times, complete displacement of the halides or halide equivalents from the group 14 centers was observed, and the new compounds $PbPh(CF_3)_3$, 51%, $PbPh_2(CF_3)_2$, 61%, $PbPh_3CF_3$, 81%, $SnPh_2(CF_3)_2$, 55%, $SnPh_3CF_3$, 80%, and $GePh_3CF_3$, 72%, were isolated and characterized. With shorter reaction times and/or with the trifluoromethylating agent as the limiting reactant, partial substitution predominated, and the new species $PbPh_2(Cl)CF_3$, 78%, $PbPh_2(O_2CCH_3)CF_3$, 89%, $PbPh(O_2CCH_3)_2CF_3$, 63%, and $PbPh(O_2CCH_3)(CF_3)_2$, 64%, were separated. In addition, two preliminary studies of the reactivity of aryl−group-IVA compounds were carried out. In the first, ligand exchanges of $PbPh_3CF_3$ with a representative main group and transition metal complex were probed; $Sb(CF_3)_3$, 61%, and $Pd(PEt_3)_2(Cl)CF_3$, 62%, were generated. In the second, the feasibility of forming aryl−CF_3 species in high yields via CuCl-mediated M−Ph cleavages was examined. In these reactions $PhCF_3$ was isolated from M_2Ph_6 in yields of 95% (M = Pb), 96% (M = Sn), and 58% (M = Ge).

Introduction

If one wishes to effect the substitution (or addition) of an alkyl or aryl substituent onto a substrate, an extremely rich and diverse array of organometallic reagents exists with which to carry out the transformation. If it is the substitution (or addition) of a CF_3 or other perfluoroalkyl group that is desired, however, the choice of reagents is much more restricted. Bis(trifluoromethyl)cadmium·glyme (glyme is 1,2-dimethoxyethane) has been shown to be reactive toward a number of transition metal and main group halides.[1] Bis(trifluoromethyl)tellurium and $Hg(CF_3)_2$ have been effectively employed in main group 14, 15, and 16 transformations[2] and the latter has been employed in oxidative-additions to late transition metals.[3] Trimethyl(trifluoromethyl)silane has been shown to be reactive, primarily toward ketones, acyl halides, and the like;[4] more recently reactions with metal fluorides have been reported.[5] The chemistry of trifluoromethyl copper has been examined in considerable detail.[6]

Although there have been many studies of alkyl group 14 species containing trifluoromethyl groups, there have been very few reports of aryl-substituted group 14 compounds that also contain CF_3 groups. This is somewhat surprising since, in general, one might expect the aryl derivatives to be more thermally and oxidatively stable than their alkyl counterparts. Additionally, the arylated species should be significantly less reactive toward nucleophilic reagents, and it seems reasonable to expect that they will ultimately be shown to exhibit reactivity patterns that are distinct from their alkylated counterparts. Prior to the inception of this work, the only trifluoromethylated group 14 aryl derivatives that had been reported were those of carbon and silicon.[7]

The objectives of this study were to synthesize the title compounds, the first series of trifluoromethylated aryl derivatives of the lower elements of group 14, to examine the variation in properties of these new compounds, and to establish, in preliminary fashion, whether these new compounds might have the potential to serve as ligand exchange reagents in their own right. For the last, a lead trifluoromethylated species was selected, in part, because lead alkyl compounds have had a long and rich history as alkyl sources and, in part, because the relatively low Pb(IV)−F bond strength might serve to discourage the difluorocarbene eliminations that have been commonly observed in other studies of metal−CF_3 reactivity. Finally, since trifluoromethylated derivatives

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10.1021/om000023m CCC: $19.00
Publication on Web 05/24/2000

Table 1. ^{19}F and ^{207}Pb NMR Data and CF_3 Analyses

	NMR data[a,b]				CF_3 analytical data				
compd	$\delta^{19}F$, ppm	$^2J(M-F)$, Hz	$\delta^{207}Pb$, ppm	$^2J(^{207}Pb-^{19}F)$ Hz	mmol compd taken	mmol CF_3H produced	%	mol CF_3I produced	%
$PbPh_3CF_3$	37.8(s)	324	−236.6(q)	323	0.350	0.347	99.1		
white solid					0.125			0.124	99.2
$PbPh_2(CF_3)_2$	40.3(s)	440	−316.0(h)	440	0.325	0.643	98.9		
white solid					0.156			0.309	99.0
$PbPh(CF_3)_3$	41.2(s)	560	−515.0(d)	557	0.176	0.528	100.0		
clear liquid					0.165			0.485	98.0
$PbPh_2(Cl)CF_3$	40.2(s)	301			0.209	0.206	98.5		
white solid									
$PbPh_2(OAc)CF_3$	40.6(s)	321			0.190	0.186	97.9		
white solid									
$PbPh(OAc)_2CF_3$	40.5(s)	349			0.272	0.271	99.6		
white solid									
$PbPh(OAc)(CF_3)_2$	39.4(s)	503			0.237	0.469	98.9		
white solid									
$SnPh_3CF_3$	31.2(s)	285/273			0.268	0.265	98.9		
white solid					0.240			0.235	97.9
$SnPh_2(CF3)_2$	30.1(s)	427/408			0.245	0.480	97.9		
white solid									
$GePh_3CF_3$	28.2(s)				0.349	0.342	98.0		
white solid					0.313			0.309	98.7

[a] M = Ge, Sn, Pb; Ph = C_6H_5, OAc = CO_2CH_3. s = singlet, h = heptet, d = decet. [b] Ext. std. for ^{19}F NMR is CF_3COOH. Ext. std. for ^{207}Pb NMR is $Pb(CH_3)_4$. $^2J(M-F) = {}^2J(^{207}Pb-^{19}F)$, $^2J(^{119/117}Sn-^{19}F)$, as appropriate.

of aromatic substances are frequently desired for the preparation of compounds of interest for medicinal or pesticide applications, the efficacy of aryl group 14 compounds for the formation of a typical trifluoromethyl aromatic species, trifluorotoluene, was assessed.

Experimental Section

General Comments. The synthesis and manipulation of air-sensitive materials were carried out in standard vacuum lines or in glovebags. Because of the toxicity of many lead compounds, rubber gloves and well-ventilated hoods were used for all benchtop procedures. All reaction times were 24 h unless otherwise noted.

Bis(trifluoromethyl)mercury[8], bis(trifluoromethyl)cadmium·glyme,[9] and $PbPh_3SEt$[10] were prepared as previously reported Other substrates were generated by standard procedures. Triphenyllead bromide (Alfa), $PbPh_2Cl_2$ (Alfa), $PbPh_2(O_2CCH_3)_2$ (Alfa), $PbPh(O_2CCH_3)_3$ (Alfa), Sn_2Ph_6 (Alfa), GeO_2 (Alfa), and PhI (Aldrich) were all used as received. Lead(II) chloride (Fisher) and CuCl (Aldrich) were heated to 130 °C under vacuum prior to use. Tetrahydrofuran was dried over sodium benzophenone ketyl. Chloroform was dried over P_2O_5; elemental iodine (Aldrich) was sublimed prior to use.

The ^{19}F (188.3 MHz), ^1H (200.1 MHz), ^{13}C (100.6 MHz), ^{31}P (181.9 MHz), and ^{207}Pb (43.8 MHz) NMR spectra were obtained at ambient temperature from samples that had been dissolved in THF or $CHCl_3$ and then sealed in 4 mm Pyrex glass tubing. Deuterium oxide was the external lock solvent. Positive chemical shifts are deshielded from external CF_3COOH (which is ca. +76.5 on the $CFCl_3$ scale), $Si(CH_3)_4$, H_3PO_4 (80%), or $Pb(CH_3)_4$, as appropriate. The 70 eV mass spectra are from quadrupole mass spectrometers. Each fragment had the correct isotopic pattern. The melting points are uncorrected. The number of CF_3 ligands in each new compound (see Table 1) was determined by hydrolysis in 0.5 M methanolic KOH. In selected cases, these analytical data were corroborated by reaction with iodine at ambient temperature in THF and/or by analyses performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Formation of $PbPh_3CF_3$. Method A. Triphenyllead bromide (0.223 g, 0.430 mmol) was mixed with 0.297 g (0.873 mmol) of $Cd(CF_3)_2$·glyme in a 100 mL round-bottomed flask equipped with a 15-cm-long neck designed such that later a coldfinger could be inserted directly into the reactor. The vessel was attached to a standard vacuum line by means of a Teflon valve and ground glass joint, evacuated, and cooled to −196 °C, and then 25 mL of THF was distilled onto the mixture. The reactor contents were warmed to ambient temperature and stirred. At the end of the reaction, all volatiles were removed by vacuum distillation at ambient temperature and discarded. The coldfinger was inserted into the reactor, which was then evacuated and heated. Triphenyl(trifluoromethyl)lead (0.177 g, 0.349 mmol), which distilled from the solid at 131 °C, was recovered from the coldfinger of the sublimation apparatus in 81.2% yield. The melting point of this compound is 127.5−128 °C.

The ^{19}F and ^{207}Pb $\{^1H\}$ NMR data and the CF_3 analyses are contained in Table 1. ^1H NMR: δ 7.2, 7.3, 7.4. IR: 692 (s), 995 (m), 1016 (w), 1109 (m), 1477 (s), 1572 (m), 2957 (s), 3067 cm^{-1} (s). MS (*m*/*e*, ion, %): 439, $PbPh_3^+$, 41.9; 431, $PbPh_2CF_3^+$, 0.8; 381, $PbPh_2F^+$, 2.6; 362, $PbPh_2^+$, 40.0; 285, $PbPh^+$, 51.1; 277, $PbCF_3^+$, 0.3; 227, PbF^+, 8.0; 208, Pb^+, 100.0; 154, Ph-Ph^+, 9.5; 77, Ph^+, 25.1; 69, CF_3^+, 5.1. Anal. Found: C 44.42, H 2.80. Calc: C 44.95, H 2.96.

Method B. Triphenythioethyllead (0.254 g, 0.509 mmol) was mixed with 0.191 g (0.561 mmol) of $Cd(CF_3)_2$·glyme and 20 mL of THF in the apparatus described above. Triphenyl(trifluoromethyl)lead (0.172 g, 0.340 mmol) was recovered in 66.8% yield. The properties of this product are identical to those reported above.

Formation of $PbPh_2(CF_3)_2$. Method A. White $PbPh_2(CF_3)_2$ (0.077 g, 0.155 mmol) was formed in 60.8% yield from the reaction (48 h) of $PbPh_2Cl_2$ (0.110 g, 0.255 mmol) with 0.172 g (0.505 mmol) of $Cd(CF_3)_2$·glyme in 25 mL of THF. This compound, which was separated as above, melts at 46 °C and volatilizes in vacuo at 52 °C.

The ^{19}F and ^{207}Pb $\{^1H\}$ NMR data and CF_3 analyses are in Table 1. ^1H NMR: δ 7.1, 7.4, 7.5. IR: 694 (s), 725 (m), 995 (w), 1261 (m), 1655 (m), 2965 (s), 3063 cm^{-1} (s). MS (*m*/*e*, ion, %): 431, $PbPh_2CF_3^+$, 26.5; 381, $PbPh_2F^+$, 34.7; 285, $PbPh^+$, 32.8; 277, $PbCF_3^+$, 0.4; 227, PbF^+, 29.5; 208, Pb^+, 100.0; 154, Ph−Ph^+, 7.0; 77, Ph^+, 16.2; 69, CF_3^+, 4.7. Anal. Found: C 34.01, H 1.88. Calc: C 33.65, H 2.00.

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Method B. Diphenylbis(trifluoromethyl)lead (0.078 g, 0.157 mmol) was recovered in 50.8% yield from the reaction of $PbPh_2(O_2CCH_3)_2$ (0.148 g, 0.309 mmol) with 0.298 g (0.876 mmol) of $Cd(CF_3)_2$·glyme and 20 mL of THF. The separation was as above.

Formation of $PbPh_2(Cl)CF_3$. Diphenyl(trifluoromethyl)lead chloride (0.069 g, 0.150 mmol) was collected in 78.1% yield from the reaction of $PbPh_2Cl_2$ (0.124 g, 0.288 mmol) with 0.065 g (0.192 mmol) of $Cd(CF_3)_2$·glyme in 25 mL of THF. The product was separated by briefly exposing the solution to air (to remove any Cd−CF_3 species), filtration, and then recrystallizion from THF. The ^{19}F NMR data and the CF_3 analyses are contained in Table 1. ^1H NMR: δ 7.4, 7.5, 7.7. MS (*m*/*e*, ion, %): 431, $PbPh_2CF_3$, 1.7; 397, $PbPh_2Cl^+$, 14.1; 285, $PbPh^+$, 23.2; 277, $PbCF_3^+$, 0.3; 243, $PbCl^+$, 45.3; 227, PbF^+, 3.5; 208, Pb^+, 100.0; 154, Ph−Ph^+, 1.6; 146, $PhCF_3^+$, 1.7; 77, Ph^+, 18.3; 69, CF_3^+, 3.8.

Formation of $PbPh_2(O_2CCH_3)CF_3$. Diphenyl(trifluoromethyl)lead acetate (0.093 g, 0.191 mmol) was collected in 89.2% yield from the reaction of $PbPh_2(O_2CCH_3)_2$ (0.164 g, 0.343 mmol) with 0.073 g (0.214 mmol) of $Cd(CF_3)_2$·glyme in 20 mL of THF. It was obtained as described immediately above.

The ^{19}F NMR data and the CF_3 analyses are contained in Table 1. ^1H NMR: δ 7.5, 7.6, 7.7, 2.0 (O_2CCH_3). MS (*m*/*e*, ion, %): 439, $PbPh_2(O_2CCH_3)F^+$, 1.6; 431, $PbPh_2CF_3^+$, 1.2; 421, $PbPh_2(O_2CCH_3)^+$, 22.9; 413, $PbPh(O_2CCH_3)CF_3^+$, 2.2; 344, $PbPh(O_2CCH_3)^+$, 2.2; 285, $PbPh^+$, 40.2; 277, $PbCF_3^+$, 0.2; 267, $PbO_2CCH_3^+$, 25.5; 227, PbF^+, 5.0; 225, $PbOH^+$, 14.2; 208, Pb^+, 100.0; 154, Ph−Ph^+, 1.9; 77, Ph^+, 4.6; 69, CF_3^+, 2.0.

Formation of $PbPh(CF_3)_3$. Phenyllead triacetate (0.195 g, 0.422 mmol) was mixed with 0.699 g (2.056 mmol) of $Cd(CF_3)_2$·glyme in a 25 mL flask. The vessel was attached to a vacuum line, evacuated, and cooled to −196 °C, and 10 mL of THF was added. After the reaction, all volatile material was fractionated with −78 and −196 °C cold traps. Phenyltris(trifluoromethyl)lead (0.106 g, 0.215 mmol) was collected from the −78 °C trap in 50.9% yield.

The ^{19}F and ^{207}Pb $\{^1H\}$ NMR data and CF_3 analyses are in Table 1. ^1H NMR: δ 7.3, 7.4, 7.5. IR: 689 (s), 727 (m), 889 (m), 995 (s), 1231 (m), 1574 (m), 3065 cm^{-1} (s). MS (*m*/*e*, ion, %): 423, $PbPh(CF_3)_2^+$, 11.3; 373, $PbPh(CF_3)F^+$, 4.0; 304, $PbPhF^+$, 2.8; 285, $PbPh^+$, 21.0; 277, $PbCF_3^+$, 1.6; 227, PbF^+, 10.4; 208, Pb^+, 100.0; 69, CF_3^+, 31.4.

Formation of $PbPh(O_2CCH_3)_2CF$. Diacetatophenyl(trifluoromethyl)lead (0.1280 g, 0.272 mmol) was formed in 62.5% yield from phenyllead triacetate (0.201 g, 0.435 mmol) and 0.135 g (0.397 mmol) of $Cd(CF_3)_2$·glyme in 20 mL of THF. It was purified as described for $PbPh_2(Cl)CF_3$.

The ^{19}F NMR data and the CF_3 analyses are in Table 1. ^1H NMR: δ 7.5, 7.6, 7.8, 2.1 (O_2CCH_3). MS (*m*/*e*, ion, %): 421, $PbPh(O_2CCH_3)_2F^+$, 4.8; 413, $PbPh(O_2CCH_3)CF_3^+$, 11.1; 403, $PbPh(O_2CCH_3)_2^+$, 7.3; 344, $PbPh(O_2CCH_3)^+$, 9.7; 285, $PbPh^+$, 11.1; 277, $PbCF_3^+$, 0.6; 267, $Pb(O_2CCH_3)^+$, 90.7; 227, PbF^+, 4.0; 225, $PbOH^+$, 20.1; 208, Pb^+, 100.0; 77, Ph^+, 46.9; 69, CF_3^+, 22.0; 59, $CO_2CH_3^+$, 2.7.

Formation of $PbPh(O_2CCH_3)(CF_3)_2$. Phenylbis(trifluoromethyl)lead acetate (0.126 g, 0.261 mmol) was collected in 63.8% yield from the reaction of $PbPh(O_2CCH_3)_3$ (0.1887 g, 0.409 mmol) with 0.418 g (1.227 mmol) of $Cd(CF_3)_2$·glyme in 20 mL of THF. This product was purified like $PbPh_2(Cl)CF_3$.

The ^{19}F NMR data and the CF_3 analysis are contained in Table 1. ^1H NMR: δ 7.5, 7.6, 7.7, 2.1 (O_2CCH_3). MS (*m*/*e*, ion, %): 423, $PbPh(CF_3)_2^+$, 8.8; 381, $PbPhCF_3CH_3C^+$, 4.3; 373, $PbPhCF_3F^+$, 2.7; 304, $PbPhF^+$, 1.8; 285, $PbPh^+$, 16.0; 277, $PbCF_3^+$, 0.9; 267, $Pb(O_2CCH_3)^+$, 1.2; 227, PbF^+, 8.0; 225, $PbOH^+$, 7.8; 208, Pb^+, 32.5; 81, CF_3C^+, 100.0.

Formation of $SnPh_3CF_3$. Triphenyl(trifluoromethyl)tin (0.134 g, 0.321 mmol) was prepared in 80.0% yield from the reaction (48 h) of 0.155 g (0.403 mmol) of $SnPh_3Cl$ with 0.142 g (0.418 mmol) of $Cd(CF_3)_2$·glyme in 30 mL of $CHCl_3$. This compound, which was purified like $PbPh_3CF_3$, above, melts at 113 °C and volatilizes in vacuo at 161 °C.

The ^{19}F NMR data and the CF_3 analyses are contained in Table 1. ^1H NMR: δ 6. 5, 6.7, 6.9. IR: 769 (s), 987 (m), 1086 (m), 1261 (m), 1630 (m), 3061 cm^{-1} (s). MS (*m*/*e*, ion, %): 401, $SnPh_3CF_2^+$, 10.0; 351, $SnPh_3^+$, 100.0; 343, $SnPh_2CF_3^+$, 3.3; 324, $SnPh_2CF_2^+$, 0.3; 274, $SnPh_2^+$, 1.2; 247, $SnPhCF_2^+$, 17.4; 197, $SnPh^+$, 51.8; 189, $SnCF_3^+$, 2.1; 139, SnF^+, 0.4; 120, Sn^+, 33.7.

Formation of $SnPh_2(CF_3)_2$. Diphenylbis(trifluoromethyl)tin (0.111 g, 0.270 mmol; mp 39 °C) was recovered in 55.0% yield from the reaction of $SnPh_2Cl_2$ (0.164 g, 0.491 mmol) with 0.201 g (0.589 mmol) of $Cd(CF_3)_2$·glyme in 15 mL of $CHCl_3$. This compound was purified as described for $PbPh_2(Cl)CF_3$, but it was recrystallized from $CHCl_3$.

The ^{19}F NMR data and the CF_3 analyses are contained in Table 1. ^1H NMR: δ 6.4, 6.6, 6.9. IR: 439 (s), 567 (m), 733 (m), 971 (s), 1094 (s), 1259 (s), 1524 (s), 1720 (s), 3044 cm^{-1} (s). MS (*m*/*e*, ion, %): 343, $SnPh_2CF_3^+$, 23.0; 305, $SnPh_2CF^+$, 19.6; 274, $SnPh_2^+$, 0.4; 266, $SnPhCF_3^+$, 25.9; 228, $SnPhCF^+$, 40.3; 197, $SnPh^+$, 10.7; 189, $SnCF_3^+$, 1.5; 154, Ph−Ph^+, 100.0; 151, $SnCF^+$, 14.8; 139, SnF^+, 0.85; 120, Sn^+, 23.8.

Formation of $GePh_3CF_3$. Triphenyl(trifluoromethyl)germanium (0.141 g, 0.377 mmol) was synthesized in 71.9% yield from the reaction of 0.178 g (0.524 mmol) of $GePh_3Cl$ with 0.285 g (0.838 mmol) of $Cd(CF_3)_2$·glyme in 10 mL of $CHCl_3$. This complex, which was purified like $PbPh_3CF_3$, above, has a melting point of 82 °C and volatilizes in vacuo at 93 °C.

The ^{19}F NMR data and the CF_3 analyses are contained in Table 1. ^1H NMR: δ 6.6, 6.8, 6.9. IR: 455 (s), 696 (m), 736 (m), 1057 (m), 1295 (m), 1589 (s), 3110 cm^{-1} (m). MS (*m*/*e*, ion, %): 324, $GePh_3F^+$, 8.9; 305, $GePh_3^+$, 0.5; 274, $GePh_2F^+$, 42.7; 259, $GePh_2CF^+$, 0.4; 228, $GePh_2^+$, 1.1; 201, $GePhCF_2^+$, 0.2; 170, $GePhF^+$, 1.4; 154, Ph-Ph^+, 100; 151, $GePh^+$, 14.9; 143, $GeCF_3^+$, 0.2; 93, GeF^+, 30.0. Anal. Found: C 61.23, H 4.05. Calc: C 61.19, H 4.03.

Interactions with $Hg(CF_3)_2$. Small amounts of the above substrates were mixed with a 2-fold excess of $Hg(CF_3)_2$ in 0.5 mL of $CHCl_3$ or THF as appropriate. After 24 h at room temperature, the mixtures were heated to 140 °C for 72 h and then to 160 °C for a further 72 h. Unreacted $Hg(CF_3)_2$ was present, but no M−CF_3 (M = Ge, Sn, Pb) linkages were observed.

Thermal Stabilities of Aryl(trifluoromethyl) Group IVA Compounds. In the absence of air, $GePh_3CF_3$ begins to decompose at ca. 90 °C, $SnPh_3CF_3$ at 162 °C, and $PbPh_3CF_3$ at 170 °C. Diphenylbis(trifluoromethyl)lead thermally decomposes at 153 °C, whereas $SnPh_2(CF_3)_2$ and $PbPh(CF_3)_3$ decompose at 106 and 90 °C, respectively. At lower temperatures, C_2F_4 (δ −56 ppm) is formed, but if heated above 200 °C, all of the compounds yield hexafluorocyclopropane (δ −79 ppm).

Preliminary Study of the Reactivity of $PbPh_3CF_3$. Reaction with SbI_3. In a 50 mL round-bottom flask equipped with an 18/9 ball joint and a Teflon valve, 1.359 g (2.678 mmol) of $PbPh_3CF_3$ was mixed with 0.396 g (0.788 mmol) of SbI_3. The reaction vessel was attached to a standard vacuum line and evacuated, and approximately 5 mL of THF was added. After 72 h at room temperature, all volatiles were fractionated with −78, −131, and −196 °C cold traps. Tris(trifluoromethyl)antimony (0.158 g, 0.480 mmol) was collected in 61.0% yield from the −131 °C trap. It was identified by ^{19}F (δ 34.1 ppm) and ^{13}C NMR (δ 130.0 ppm, $J_{^{13}C-^{19}F} = 356$ Hz) spectra.[2a,b]

Reaction with $Pd(PEt_3)_2Cl_2$. Triphenyl(trifluoromethyl)lead (1.091 g, 2.151 mmol) was mixed with 0.903 g (2.188 mmol) of $Pd(PEt_3)_2Cl_2$. The vessel was attached to a standard vacuum line and evacuated, and 25 mL of THF was added. After stirring for 48 h at ambient temperature, all volatiles were removed. Pale yellow $Pd(PEt_3)_2(Cl)CF_3$ (0.595 g, 1.334 mmol), 62.0% yield, sublimed at 85 °C. The ^{19}F NMR (CH_2Cl_2) is a triplet at δ 66.9 ppm $^3J_{^{31}P-^{19}F} = 35.7$ Hz. The $^{31}P\{^1H\}$

NMR spectrum is a quartet at δ 25 ppm $J_{^{31}P-^{19}F}) = 35$ Hz. The melting point of the compound is 75 °C.[11]

Reaction of Pb_2Ph_6, Sn_2Ph_6, and Ge_2Ph_6 with $Cd(CF_3)_2$·Glyme in the Presence of CuCl. In a 10 mm × 10 cm reactor, 0.0116 g (0.013 mmol) of Pb_2Ph_6 was mixed with 0.0135 g (0.039 mmol) of $Cd(CF_3)_2$·glyme and 0.0078 g (0.078 mmol) of CuCl. The reactor was evacuated and cooled to −196 °C, and 5 mL of THF was added. In a second reactor 0.0108 g (0.015 mmol) of Sn_2Ph_6 was combined with 0.0158 g (0.046 mmol) of $Cd(CF_3)_2$·glyme, 0.0089 g (0.090 mmol) of CuCl, and 5 mL of THF. In a third reactor 0.0122 g (0.020 mmol) of Ge_2Ph_6 was mixed with 0.0205 g (0.060 mmol) of $Cd(CF_3)_2$·glyme, 0.0119 g (0.120 mmol) of CuCl, and 5 mL of THF.

After 7 days at room temperature, all volatiles were removed from the red, dark gray, and white solids and then carefully fractionated. No compounds with $M-CF_3$ (M = Ge, Sn, Pb) linkages were recovered from the solids or volatiles. Trifluoromethylbenzene (0.0108 g, 0.074 mmol) was recovered in 95% yield from the lead reaction. From the tin reaction $PhCF_3$ (0.0126 g, 0.086 mmol) was recovered in 96% yield. From the germanium reaction $PhCF_3$ (0.0102 g, 0.070 mmol) was isolated in 58% yield. Trifluoromethylbenzene was characterized by mass spectrometry (*m/e*, ion, %: 146, $PhCF_3^+$, 100; 127, $PhCF_2^+$, 94.2; 96, PhF^+ 69.8) along with ^{19}F (δ 15.7 ppm), $^{13}C\{^1H\}$ (δ 124, 127, 129.4, 130.6, 133.6 (CF_3, q)), and ^1H NMR (δ 6.6, 6.9, 7.1 ppm) spectroscopy.

Interaction of Pb_2Ph_6, Sn_2Ph_6, and Ge_2Ph_6 with $Hg(CF_3)_2$ in the Presence of CuCl. The reactivity of 20 mmol samples of Pb_2Ph_6, Sn_2Ph_6, and Ge_2Ph_6 toward 60 mmol $Hg(CF_3)_2$ in the presence of 120 mmol CuCl and THF was similarly monitored at ambient temperature and 100, 120, and 146 °C by ^{19}F and ^1H NMR spectroscopy. No reaction was observed after 3 months at ambient temperature; only trace amounts of $PhCF_3$ were observed from the lead and tin reactions after 72 h at 146 °C.

Results and Discussion

Synthesis. All of the lower group IVA aryl derivatives tested are reactive toward $Cd(CF_3)_2$·glyme at ambient temperature; the lead reactions were best carried out in THF, but $CHCl_3$ was superior for the Sn and Ge complexes. In general, the CF_3 substitutions of the lead complexes proceed slightly faster than the reactions of the analogous derivatives of the other elements. The yields were good, ca. 50% to ca. 90%, and the separations were straightforward. Because of the limited thermal stability of the Pb(IV) halides, SC_2H_5 and O_2CCH_3 ligands were briefly examined as potentially superior leaving groups, but no advantages were apparent. The acetate ligand, while reactive, has the disadvantage that two $Cd-CF_3$ groups are required since the first forms CH_3COF, and it is only the second that appears as a $Pb-CF_3$ ligand.

The relatively lengthy reaction times were adopted after preliminary experiments demonstrated that the trifluoromethylation of aryl-substituted group IVA compounds by the $CdCF_3$ reagent is much slower than that of the tetrahalides. For example, 48 h was needed for the reaction of $SnPh_3Cl$, much longer than the 1−2 h necessary for $SnBr_4$ or GeI_4.[9a] Similarly, the reactions of GeI_4 and $SnBr_4$ with $Hg(CF_3)_2$ have been shown to generate trifluoromethyl Ge and Sn compounds,[2c,12] but at temperatures up to 120 °C, no reaction between $Hg(CF_3)_2$ and the aryl derivatives examined here was observed.

One advantage of the slower trifluoromethylations of the aryl-containing group 14 substrates is that partial substitution can be readily carried out to generate products such as $PbPh_2(O_2CCH_3)CF_3$ in good yield (89%). In the absence of electrophiles such as HCl and CuCl (see below), the group 14−Ph bonds are unaffected by the trifluoromethylation procedures employed. In contrast, however, methyl substituents bonded to these elements readily react with $Hg(CF_3)_2$ or $Cd(CF_3)_2$·glyme to form group $14-CF_3$ derivatives.[13]

All of the trifluoromethyl aryl compounds formed here are colorless substances that are reasonably thermally stable, with the stability for analogous compounds decreasing in the order Pb > Sn > Ge. For example, the MPh_3CF_3 species decompose at 170, 162, and 110 °C for M = Pb, Sn, and Ge, respectively. Since the mean thermochemical M−C bond enthalpies are in the opposite order,[14] these temperatures may indeed reflect the relative ease with which CF_2 elimination occurs. The mixed ligand species, e.g., $PbPh(OAc)_2CF_3$, however, are much more thermally sensitive.

Upon exposure to the atmosphere, the lead compounds were the least reactive, with the tin and germanium derivatives increasingly more air sensitive. Indeed, the compounds $PbPh_3CF_3$ and $PbPh_2(CF_3)_2$ are remarkably stable toward air; they both persist for well over a year seemingly unaffected. The others react within minutes or, at most, a few hours.

Characterization. The spectroscopic data are all in accord with the formulation of the compounds as indicated. For example, as expected, the ^{19}F chemical shifts for the MPh_3CF_3 series (δ = 37.8, 31.2, and 28.2 ppm for M = Pb, Sn, and Ge) become slightly more shielded as the central element becomes located more toward the top of the periodic table. Presumably because of the increasing amount of s character in the $Pb-CF_3$ bond as CF_3 groups are substituted for Ph groups, $^2J(^{207}Pb-^{19}F)$ increases from 323 to 557 Hz for the series $PbPh_n(CF_3)_{4-n}$, n = 1, 2, 3 (see Table 1), and for $SnPh_2(CF_3)_2$ relative to $SnPh_3CF_3$ (see Table 1). Although the ^1H (see Experimental Section) and ^{19}F chemical shifts are relatively insensitive to CF_3 for Ph substitutions, $\delta^{207}Pb$ is not. Here, the resonances become much more shielded after each CF_3 for Ph substitution (see Table 1). In the $^{207}Pb\{^1H\}$ NMR spectra, the $PbPh_3CF_3$ and $PbPh_2(CF_3)_2$ resonances are a quartet and a heptet as anticipated, but only 8 of the 10 lines expected in the $^{207}Pb\{^1H\}$ NMR spectrum of $PbPh(CF_3)_3$ are unequivocal. However, the calculated intensity of the outermost two lines that would complete the expected decet is only 0.4% of the total.

As is typical for tetravalent group IVA compounds, molecular ions were not observed in the mass spectra, but the expected fragmentation patterns, e.g., $PbPh_2CF_3^+$ and $PbPh_3^+$ ions in the $PbPh_3CF_3$ spectrum, are evident. Each of the group IVA-containing ions had the

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appropriate isotopic abundance. All of the infrared spectra contain absorptions characteristic of monosubstituted phenyl rings and CF_3 groups.

Preliminary Reactivity Studies. One reason that the reactivity of $PbPh_3CF_3$ was assessed is that in contrast to $SiMe_3CF_3$ (and some of the complexes prepared here), $PbPh_3CF_3$ is stable in air for very long periods. Because of their extended shelf lives, $PbPh_3CF_3$ and $PbPh_2(CF_3)_2$ might prove to be very convenient, easily stored, and readily accessible trifluoromethylating agents.

To begin to examine the reactivity of $PbPh_3CF_3$, its reactions with a representative main group and transition metal halide were explored. The fully trifluoromethylated antimony(III) compound, $Sb(CF_3)_3$, was easily prepared at ambient temperature in 61% yield. Previous syntheses, which have typically required prolonged heating of CF_3I, $Hg(CF_3)_2$, or $Te(CF_3)_2$ with Sb or SbI_3 in a bomb reactor,[2ab,15] are much less convenient. The reaction of the palladium complex $Pd(PEt_3)_2(Cl)_2$ with $PbPh_3CF_3$ generated the monosubstituted $Pd(PEt_3)_2(Cl)CF_3$, which was separated in good yield, 62%, after 48 h at ambient temperature. These results indicate that the monosubstituted lead compound $PbPh_3CF_3$ is more reactive than $Hg(CF_3)_2$ but less reactive than $Cd(CF_3)_2{\cdot}$glyme. Presumably, the disubstituted compound $PbPh_2(CF_3)_2$ will prove to be more reactive than $PbPh_3CF_3$. The reactions of the disubstituded species are currently under study.

The interactions of the M_2Ph_6 species, M = Pb, Sn, and Ge, with $Cd(CF_3)_2{\cdot}$glyme were designed to examine whether trifluoromethylated aromatic compounds could be easily prepared in this system or if the M−M bond would be cleaved to form, for example, $GePh_3CF_3$ instead. In the absence of CuCl or other similar reagents no cleavage of the metal(oid)−Ph bond was found, but in the presence of CuCl, trifluorotoluene was formed in yields that ranged from 95+% for Pb and Sn to 58% for Ge. The mechanism of this reaction is under investigation, but the current results are not inconsistent with transmetalation to yield CuPh followed by a radical step involving Cd−CF_3 to generate $PhCF_3$, Cu (the red solid observed), and Cd. Presumably, it is the more readily oxidized Cd that intercepts any halogen released by, for example, Pb(II).

One advantage of the reactions shown here *vis-à-vis*, for example, typical $CuCF_3$ aryl trifluoromethylations is that the formation of the trifluoromethyl aromatic derivative readily proceeds at ambient temperature and pressure rather than the elevated temperatures and pressures that are commonly required with alternative methodology.[6,16] In addition, the less expensive aryl bromides can be employed to form the M_2Ph_6 substrates rather than the aryl iodides that have typically been used with $CuCF_3$. Currently the price of a mole of PhI from one major supplier (Aldrich) is about 8 times that of PhBr and ca. 18 times that of the chloride. The scope of this reaction is also under further investigation.

In conclusion, we have prepared and separated a series of trifluoromethylated derivatives of aryl-containing group 14 elements by means of reactions with $Cd(CF_3)_2{\cdot}$glyme and found that, once formed, the aryl-containing trifluoromethyl compounds are reasonably thermally and oxidatively robust. We have also shown that one of these compounds, $PbPh_3CF_3$, is an active trifluoromethyl transfer agent which readily forms main group, transition metal, and aromatic derivatives.

Acknowledgment. The financial contributions of the National Science Foundation are gratefully acknowledged.

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