

Trifluoromethyl Group 2B Compounds: Bis(trifluoromethyl)cadmium·Base. New, More Powerful Ligand-Exchange Reagents and Low-Temperature Difluorocarbene Sources

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Abstract: Lewis base adducts of bis(trifluoromethyl)cadmium have been isolated from the interaction of bis(trifluoromethyl)mercury with dimethylcadmium in solvents like THF, glyme, diglyme, or pyridine. Lewis base exchange, for example, pyridine for glyme, occurs upon dissolution of the glyme adduct, $(\text{CF}_3)_2\text{Cd}\cdot\text{g}$, $\text{g} = \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$, in pyridine. The $(\text{CF}_3)_2\text{Cd}\cdot\text{base}$ species are shown to be much more reactive than $(\text{CF}_3)_2\text{Hg}$ since the cadmium compounds are reactive at temperatures at least 100 °C below that required for the mercurial. At ambient temperatures ligand exchanges between SnBr_4 or GeI_4 and $(\text{CF}_3)_2\text{Cd}\cdot\text{glyme}$ are found to be most convenient preparations of $(\text{CF}_3)_4\text{Sn}$ (66% yield) or $(\text{CF}_3)_4\text{Ge}$ (43% yield); the formation of $(\text{CF}_3)_3\text{P}$ from the reaction of PI_3 also occurs, but the amounts isolated are smaller. The reaction of acyl halides with $(\text{CF}_3)_2\text{Cd}\cdot\text{g}$ proceeds at subambient temperature to yield the acyl fluoride, ca. 90% yield, and difluorocarbene which can be trapped stereospecifically by, e.g., *cis*-2-butene at -30 °C. Difluorocarbene formation occurs at temperatures at least as low as -78 °C.

Although a number of organometallic compounds that contain perfluoroalkyl groups have been shown to be approximately as thermally stable as the analogous perhydrogenated alkyl derivatives,^{1,2} the chemistry of σ -bonded perfluoroalkyl organometallic compounds has always lagged far behind that of the corresponding hydrogen-containing species. One reason for the disparity in the amount of information currently available about these two systems is that at present there are only a few intermediaries which are known to transform metallic or metalloid substrates into perfluoroalkyl derivatives whereas any of a great number of diverse alkylating agents of widely varying reactivity can be selected for the synthesis of a designated hydrogen-containing organometallic compound.

Almost all of the early preparations of perfluoroalkylated organometallic compounds utilized only one reagent, CF_3I , which was then one of the few fluoroalkyl sources that was easily prepared and controllably reactive. The "first generation" experiments resulted in the formation of fully substituted derivatives of many of the relatively electronegative elements of groups 5 and 6A as well as a few compounds where more electropositive elements had been mono- or disubstituted with perfluoroalkyl groups. For example, species like $\text{CF}_3\text{Sn}(\text{CH}_3)_3$, CF_3GeI_3 , and $(\text{CF}_3)_2\text{GeI}_2$ from the main-group elements or $\text{CF}_3\text{Fe}(\text{CO})_4\text{I}$ and $\eta^5\text{-C}_5\text{H}_5\text{Co}(\text{CO})\text{CF}_3(\text{I})$ from the transition-metal elements were prepared by reaction with CF_3I .³

Further developments in this field, however, required a second generation of experimental techniques which relied upon more advanced technology to achieve higher degrees of substitution or, for transition-metal compounds, derivatives less encumbered by other ligands. The more recent experiments have involved innovations such as the reactions of CF_3I with metal atoms,¹ or the reactions of CF_3 radicals—generated from C_2F_6 by radio frequency discharge—with metallic halides,^{4,5} or metal atoms.⁶ These experiments, which have been recently reviewed,^{1,7} have resulted in the first preparation of fully substituted trifluoromethyl de-

derivatives of a number of the more electropositive main-group elements, e.g., $(\text{CF}_3)_4\text{Ge}$, $(\text{CF}_3)_4\text{Sn}$, $(\text{CF}_3)_3\text{Bi}$, and $(\text{CF}_3)_2\text{Te}$, and in the formation of partially substituted transition-metal compounds, like CF_3PdI ,¹ where other ligands previously thought to be required were found to be unnecessary. Direct fluorination techniques have also been reported. In some instances the last method does yield the fully substituted trifluoromethyl compound, but often the formation of metal fluorides results instead. For example, $(\text{CF}_3)_2\text{SnF}_2$ was formed in the fluorination of $\text{Sn}(\text{CH}_3)_4$ rather than $(\text{CF}_3)_4\text{Sn}$.⁷

Thus until recently one very serious difficulty in the preparation of many perfluorinated organometallics and the study of their reactivity has been that relatively sophisticated, and expensive, equipment has been required to prepare many species of interest. If, however, perfluoroalkyl-containing organometallic compounds are as stable thermally as has often been suggested, it would seem that there should exist at least one synthetic route which could be utilized for the preparation of a broad spectrum of fluoroalkyl species, a route which would require only commonly available reagents and materials.

One seemingly obvious synthetic technique that has not been studied in detail, presumably due to some erroneous early reports, is the ligand-exchange reaction of metal halides or pseudohalides with group 2B bis(trifluoromethyl)metal compounds. Recently, however, $(\text{CF}_3)_2\text{Hg}$ has been shown to exchange ligands with the halides of several main-group elements, e.g., Ge, Sn, and P, and these reactions have been shown to result in convenient preparations of a number of partially substituted compounds like $(\text{CF}_3)_3\text{GeI}$, in 70% yield, or CF_3SnBr_3 , in 50% yield.^{8,9} Reactions utilizing the mercurial, however, require temperatures exceeding 100 °C and reaction times of at least hours and more often days, conditions that have been shown to be incompatible with extensive or complete trifluoromethylation of many of the more electropositive elements, for example, tin.^{10,11}

The preparation of the related group 2B trifluoromethyl compound, $(\text{CF}_3)_2\text{Cd}$, has been attempted numerous times.¹²⁻¹⁵ NMR

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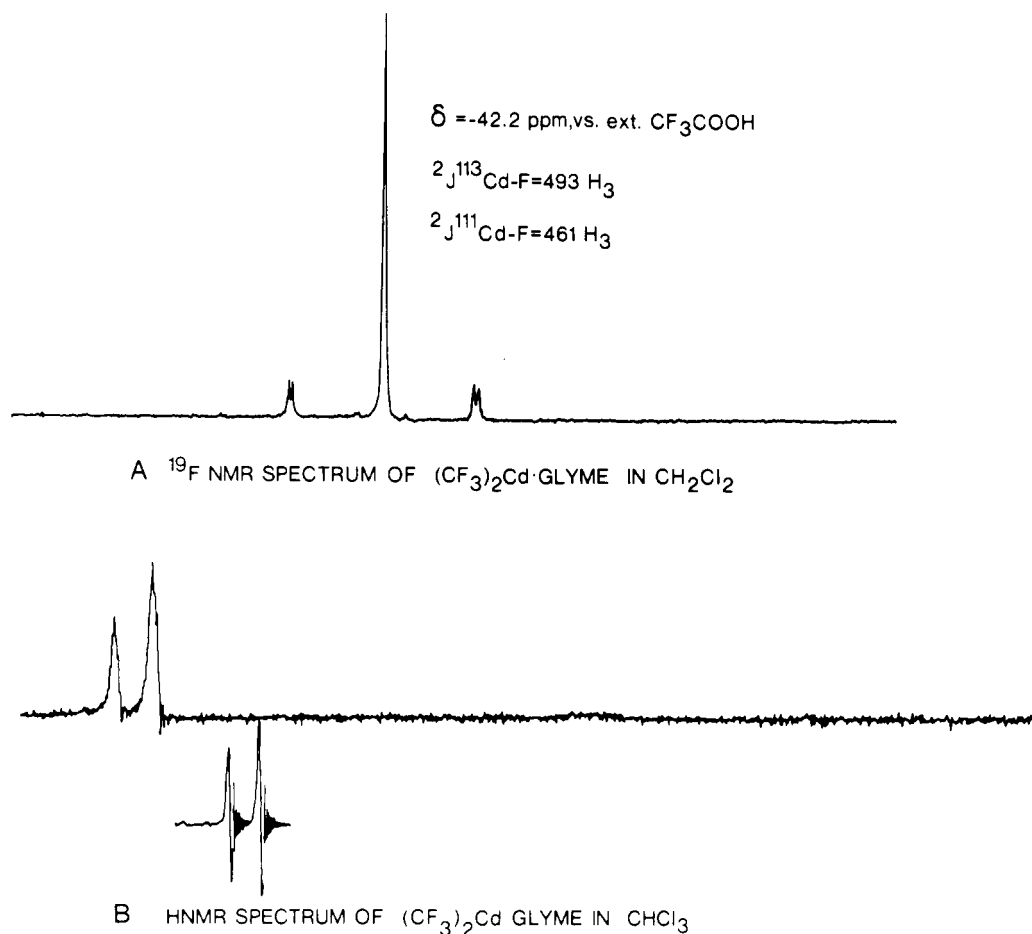


Figure 1. A: fluorine NMR of $(\text{CF}_3)_2\text{Cd}$ -glyme after removal of volatile materials; see text. B: upper trace, broadened and deshielded resonances of complexed glyme (PMR); lower trace, uncomplexed glyme in CHCl_3 (PMR).

absorptions observed during the interaction of $(\text{CF}_3)_2\text{Hg}$ with $\text{Cd}(\text{CH}_3)_2$ in pyridine were attributed to the presence of $(\text{CF}_3)_2\text{Cd}$,^{14,15} but neither this reagent nor any Lewis base adducts of $(\text{CF}_3)_2\text{Cd}$ have ever been isolated and characterized. The purpose of the present investigation was to determine whether the disubstituted cadmium compound, $(\text{CF}_3)_2\text{Cd}$, or its adducts, $(\text{CF}_3)_2\text{Cd}\cdot\text{L}_n$ could be formed, isolated, and characterized and to then ascertain whether some or all of these compounds might not be much more powerful ligand-exchange reagents than $(\text{CF}_3)_2\text{Hg}$.

The formation and isolation of several Lewis base adducts of $(\text{CF}_3)_2\text{Cd}$ and the first examples of the utility of these (trifluoromethyl)cadmium species in ligand exchanges are reported. By means of a series of reactions with inorganic halides the glyme-containing cadmium reagent is shown to be a much more powerful ligand-exchange reagent than is $(\text{CF}_3)_2\text{Hg}$. Finally, in the reaction of acyl halides with $(\text{CF}_3)_2\text{Cd}$ -glyme, glyme = $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$, the acyl fluoride is shown to form at subambient temperatures, while CF_2 transfer is demonstrated by the isolation of the expected difluorocyclopropanes formed stereospecifically from alkenes which had been added to the reaction mixture.

Experimental Section

General Procedures. Except where noted all manipulations were carried out with the aid of a standard vacuum line in order to ensure the absence of air and water. Proton NMR spectra were obtained at 60 MHz; positive chemical shifts are deshielded relative to external tetramethylsilane. Fluorine magnetic resonance data are from a Bruker HFX-90 spectrometer operating at 84.7 MHz; positive chemical shifts are shielded relative to the external standard, trifluoroacetic acid. Mass spectra were recorded on an AEI MS 30 instrument typically operating at an ionization potential of 70 eV and ambient temperature. IR data

Table I. Isolated Yield of $(\text{CF}_3)_2\text{Cd}\cdot\text{Glyme}$ as a Function of Reaction Time^a

time, min	yield, %	$(\text{CF}_3)_2\text{Cd}\cdot\text{glyme}$ formed, mmol
20	11.4	0.529
50	43	2.76
130	60	8.88
140	57	5.79
1140	54	6.67

^a $(\text{CF}_3)_2\text{Hg}$ in ca. 20% excess; yields based upon $\text{Cd}(\text{CH}_3)_2$, see text.

are from a PE 521 spectrophotometer.

Dimethylcadmium was obtained commercially or prepared from the interaction of CdI_2 with methyl Grignard. Bis(trifluoromethyl)mercury was formed by the thermal decarboxylation of mercury trifluoroacetate.⁹ Solvents were dried over sodium benzophenone ketyl or calcium hydride. Inorganic iodides were resublimed prior to use; acyl halides were secured commercially and used as obtained.

Preparation of Lewis Base Adducts of $(\text{CF}_3)_2\text{Cd}$. The bis(trifluoromethyl)cadmium adducts were prepared by ligand-exchange reactions of $(\text{CF}_3)_2\text{Hg}$ with $\text{Cd}(\text{CH}_3)_2$, utilizing the desired base as solvent and reagent. For the preparation of $(\text{CF}_3)_2\text{Cd}$ -glyme, for example, $(\text{CF}_3)_2\text{Hg}$, 4.20 g (12.43 mmol), was dissolved in 5.0 mL of dried glyme. Under vacuum 1.44 g (10.14 mmol) of $\text{Cd}(\text{CH}_3)_2$ was added, and the solution was then magnetically stirred for 2.3 h; during this time the solution slowly turned cloudy. Bis(trifluoromethyl)cadmium-glyme, 1.97 g (5.79 mmol), is easily purified by prolonged pumping (ca. 12 h) under vacuum which removes unreacted reagents, solvent, $\text{Hg}(\text{CH}_3)_2$, and CF_3HgCH_3 , from the vessel. As shown in Table I, at ambient temperature the isolated yield of the product approaches 60% only after reaction times near 2 h; slow decomposition of the material does occur in solution, as indicated by the yields in Table I.

When dissolved in, e.g., methylene chloride, the ^{19}F NMR spectrum of the white solid which remains after the removal of the volatile materials from the reactor, see Figure 1, consists of a singlet, $\delta = -42.2$, symmetrically surrounded by the expected ^{113}Cd and ^{111}Cd satellites; no other

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Table II. Characterization of Products from (CF₃)₂Cd·Glyme Reactions

A. Inorganic Species				
compd	¹⁹ F NMR, ^a ppm	J _{M-F} , Hz		mass spectrum ^h
(CF ₃) ₄ Sn	-38.8	537, 514		377, (CF ₃) ₃ SnCF ₂ (15%) 327, (CF ₃) ₃ Sn (51%)
(CF ₃) ₃ SnBr	-36.3	678, 656		337, (CF ₃)CF ₂ SnBrF (20%) 287, CF ₃ SnF ₂ Br (10%)
CF ₃ SnBr ₃	-29.8	868, 822		413, CF ₂ SnBr ₃ (11%) 363, SnBr ₃ (100%)
(CF ₃) ₄ Ge	-27.4			331, (CF ₃) ₃ GeCF ₂ (8%) 281, (CF ₃) ₃ Ge (44%)
(CF ₃) ₃ GeCH ₃ ^b	-24.0			277, (CF ₃) ₂ CH ₂ GeCF ₂ (30%) 227, (CF ₃) ₂ CH ₃ Ge (80%)
(CF ₃) ₃ GeI	-23.4			9
(CF ₃) ₃ P	-24.4	83 ^c		
(CF ₃) ₂ PI	-22.9	76		296, (CF ₃) ₂ PI (9%) 277, (CF ₃)CF ₂ PI (5%)
PF ₃	-44.3	1402 ^d		
(CF ₃) ₂ Cd·g	-42.2	493, 461		273, CF ₃ Cd·g (65%) 223, FCd·g (70%)
(CF ₃) ₂ Cd·dg	-44.1	471, 448		367, CF ₃ CF ₂ Cd·dg (35%) 317, CF ₃ Cd·dg (43%)
(CF ₃) ₂ Cd·2py	-46.7	374, 354		391, CF ₃ CF ₂ Cd·2py (32%) 341, CF ₃ Cd·2py (100%)
(CF ₃) ₂ Cd·2THF	-44.5	476, 457		233, CF ₃ CdCF ₂ (56%) 114, Cd (100%)
B. Organic Species				
compd	¹⁹ F NMR, ppm	¹ H NMR, ppm	J _{H-F} , Hz	mass spectrum ^h
C ₆ H ₅ C(O)F	-96.7			124, C ₆ H ₅ COF (69%) 105, C ₆ H ₅ CO (31%)
CH ₃ C(O)F	-125.5	1.53	7.5	62, CH ₃ COF (95%) 47, COF (95%)
C ₂ F ₄	+56.7			100, C ₂ F ₄ (38%) 81, C ₂ F ₃ (94%)
CF ₃ I	-71.2			196, CF ₃ I (94%) 177, CF ₂ I (35%)
CH ₃ I		2.53		142, CH ₃ I (100%) 141, CH ₂ I (30%)
(CH ₃) ₂ CCF ₂ C(CH ₃) ₂	+70.4 ^e	0.84	2.1	134, C ₆ H ₅ F ₂ (16%) 119, C ₆ H ₅ F ₂ (100%)
<i>c</i> -CH ₃ CHCF ₂ CH(CH ₃)	+47.5, +76.5	1.4, 0.97	<i>f</i>	
<i>t</i> -CH ₃ CHCF ₂ CH(CH ₃)	+63.8		0	

^a Positive values shielded relative to external CF₃COOH. ^b ¹H NMR, δ 0.75. ^c Lit. δ -25.7; *J* = 83 Hz. ^d ³¹P NMR, *J* = 1400 Hz; lit. δ -43.4. ^e Nine of expected thirteen resonances observed. ^f ⁴*J*_{HF} = 3 Hz; ³*J*_{HF} = 15 Hz; ²*J*_{FF} = 151 Hz. ^g lit. δ +65.8; see R. A. Mitsch, *J. Am. Chem. Soc.*, 87, 758 (1965). ^h *m/e*, ion (ion abundance).

resonances are observed in the fluorine NMR. As shown in Figure 1, aside from the solvent, the only resonances found in the ¹H NMR are due to complexed glyme, δ 4.18 (CH₂) and δ 4.00 (CH₃), whereas for uncomplexed glyme, δ 3.63 (CH₂) and 3.48 (CH₃). Infrared absorptions occur at 2958 (s), 2922 (s), 2865 (m), 1405 (m), 1398 (m), 1393 (m), 1262 (m), 1130 (s), 1122 (s), 1112 (s), 1020 (s), 865 (w), 805 (s), 755 (m), 695 (m), 680 (m), 670 (m) cm⁻¹.

With the spectrometer operating at ambient temperature, the mass spectrum of the (CF₃)₂Cd·glyme adduct melt the following, *m/e*, ion (ion abundance): 273, CF₃Cd·g (65%); 223, CdF·g (70%); 204, Cd·g (10%); 202, CF₃CdF (7%); 183, CF₃Cd (25%); 129, CdCH₃ (20%); 114, Cd (100%). With the ionization chamber at 90 °C, however, the mass spectrum contains the following, *m/e*, ion, (ion abundance): 273, CF₃Cd·g (11%); 223, FCd·g (15%); 208, FCdO(CH₂)₂OCH₃ (15%); 193, FCd(OCH₂)₂ (15%); 183, CF₃Cd (15%); 148, FCdCH₃ (26%); 129, CdCH₃ (100%); 114, Cd (100%) (where *g* is glyme).

When sealed into capillary tubes under dry nitrogen, the glyme adduct is observed to melt with decomposition at 81 °C. Hydrolysis of (CF₃)₂Cd·glyme (0.5312 g (1.561 mmol)) isolated as indicated above, results in the formation of CF₃H (0.2028 g (2.897 mmol)) along with the release of glyme (0.1343 g (1.492 mmol)) which corresponds to the formulation of the species as [(CF₃)_{0.93}]₂Cd·glyme_{0.96}.

Bis(trifluoromethyl)cadmium·glyme is soluble in many common solvents such as glymes, ethers, and haloalkanes, is insoluble in alkanes like pentane, and is only sparingly soluble in arenes like benzene or toluene. The material may be routinely handled in air for short periods, although if the above separation is incomplete ignition of the impure sample is observed. The reagent is best stored at lower temperatures since thermal decomposition does slowly occur at ambient temperature.

Many other Lewis base adducts of (CF₃)₂Cd can easily be prepared and isolated by a procedure analogous to that indicated above. The length of time required for the solutions to achieve equilibrium, however, varies with the nature of the base used. For example, as shown in Figure 2, equilibrium in THF is reached only after ca. 19 h. In diglyme or pyridine the reactions proceed much faster, requiring only a few minutes. Typical isolated yields are 60–70%, except for THF, which are 40–50%.

The physical properties of all of the adducts are similar, although, of course, small variations are observed; for example, in the fluorine NMR the chemical shift of the (di)pyridine adduct in pyridine is -46.7 ppm with coupling constants of 374, 354 Hz, while the chemical shift of the diglyme adduct in dibromoethane is -44.1 ppm with coupling constants of 471, 448 Hz; see Table II. The reaction of (CF₃)₂Hg with Cd(CH₃)₂ in the protic solvents H₂NC₂H₅ or HN(C₂H₅)₂ results in the formation of CF₃HgCH₃ and Hg(CH₃)₂ but, as yet, has not afforded isolatable (trifluoromethyl)cadmium containing exchange products.

Lewis Base Exchange. Alternatively, a desired (CF₃)₂Cd adduct may be synthesized by Lewis base exchange. For example, if dimethyltellurium is added in 20-fold excess to (CF₃)₂Cd·glyme, 0.1 g, the proton NMR of the solution indicates that the glyme present is not complexed to the cadmium since the chemical shifts of the methyl and methylene groups are identical with those obtained from a solution of glyme in Te(CH₃)₂ and the characteristic broadening of the resonances of complexed glyme (see Figure 1) is not observed. In the fluorine NMR the chemical shift of the trifluoromethyl group is found to be -50.9 ppm while ²*J*_{Cd-F} is 401, 384 Hz. Trifluoromethane is not formed in this reaction.

Similarly, (CF₃)₂Cd·glyme (0.1 g) in the presence of excess pyridine forms the pyridine adduct as evidenced by the fluorine NMR spectrum,

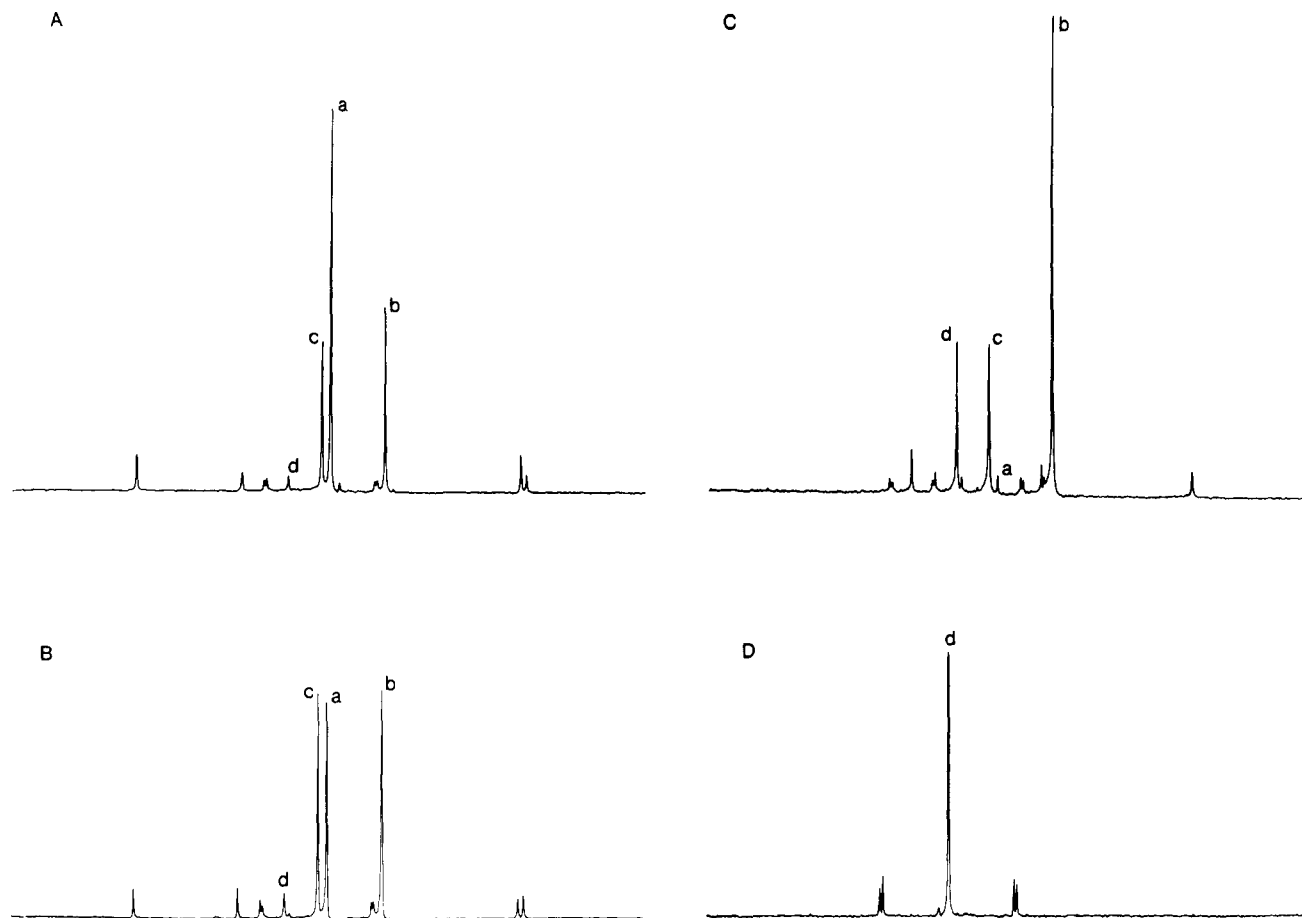


Figure 2. Fluorine NMR of reaction between excess $(\text{CF}_3)_2\text{Hg}$ and $\text{Cd}(\text{CH}_3)_2$ in tetrahydrofuran: A, after 2.5 h; B, after 7 h; C, after 25 h; D, $(\text{CF}_3)_2\text{Cd} \cdot (\text{THF})_2$ in $\text{BrCH}_2\text{CH}_2\text{Br}$ after removal of all volatile material; see text. Labeled resonances: a, $(\text{CF}_3)_2\text{Hg}$; b, CF_3HgCH_3 ; c, CF_3CdCH_3 ; d, $(\text{CF}_3)_2\text{Cd}$. Smaller singlets are due to ^{199}Hg -F coupling; smaller apparent doublets are due to $^{113/111}\text{Cd}$ -F coupling.

(δ -46.6 ppm ($^2J = 374, 359$ Hz)) and mass spectrum, the latter containing ions corresponding to the molecular ions less fluorine and CF_3 . The isolated yield of $(\text{CF}_3)_2\text{Cd}$ -pyridine is 96%.

Reactions of $(\text{CF}_3)_2\text{Cd}$ -Base with Representative Inorganic Halides. The reactions indicated below were carried out in a 150-mL three-necked flask, one neck of which was connected through a removable stopcock to the vacuum system. Another neck of this flask was fitted with a Pyrex tube (20-mm o.d.) which had been sealed at one end and bent at a 90° angle in the middle; the third neck was plugged. Either $(\text{CF}_3)_2\text{Cd}$ -base or the halide could be placed in the ear and added at a predetermined rate to magnetically stirred solutions containing the other reagent by slight rotations of the tube. The apparatus was preassembled in a nitrogen atmosphere, fitted to the vacuum system, cooled by a liquid nitrogen bath, and evacuated. When the mixture was warmed to ambient temperature, the reactants were combined as indicated below. Any volatile materials formed including the (trifluoromethyl) main-group products were later separated by trap to trap fractionation.

Reaction of $(\text{CF}_3)_2\text{Cd}$ -Glyme with SnBr_4 . Over a period of 2 h bis-(trifluoromethyl)cadmium-glyme (1.077 g (3.15 mmol)) was added in small portions to a solution of 1,6-dibromohexane (7 mL), which contained 7.489 g (17.02 mmol) of SnBr_4 . Each addition of $(\text{CF}_3)_2\text{Cd}$ -glyme resulted in the vigorous production of gaseous material. Throughout the reaction, the flask was constantly vented to the vacuum system to ensure the immediate removal of all volatile materials produced.

After 3 h, fractionation of the volatile products indicated the formation of $(\text{CF}_3)_4\text{Sn}$ (0.354 g (0.89 mmol)), $(\text{CF}_3)_3\text{SnBr}$ (0.042 g (0.10 mmol)), and CF_3SnBr_3 (0.063 g (0.15 mmol)). Small amounts of CH_3I and C_2F_4 were also isolated and identified. After 2 more hours or reaction $(\text{CF}_3)_4\text{Sn}$ (0.056 g (0.14 mmol)), a very small amount of $(\text{CF}_3)_3\text{SnBr}$, and CF_3SnBr_3 (0.210 g (0.49 mmol)) had formed. Free glyme was not observed in the volatile materials recovered. The overall yields for the (trifluoromethyl)stannanes, on the basis of $(\text{CF}_3)_2\text{Cd}$ -glyme, were 66% for $(\text{CF}_3)_4\text{Sn}$, 5% for $(\text{CF}_3)_3\text{SnBr}$, and 10% for CF_3SnBr_3 . See Table II for product characterization.

If, however, a slight excess of $(\text{CF}_3)_2\text{Cd}$ -glyme was quickly added to SnI_4 (3 mmol) in CH_2Cl_2 , separation after 15 min indicated the formation of large amounts of C_2F_4 accompanied by smaller amounts of CH_3I .

(Trifluoromethyl)tin containing species volatile at ambient temperature were not isolated. After removal of the solvent, interaction of the solids remaining with $\text{Cd}(\text{CH}_3)_2$ liberated $\text{CF}_3\text{Sn}(\text{CH}_3)_3^{10}$ and $(\text{CF}_3)_2\text{Sn}(\text{CH}_3)_2^{10}$ in 23 and 10% yield, respectively, along with $\text{Sn}(\text{CH}_3)_4$.

Reaction of $(\text{CF}_3)_2\text{Cd}$ -Glyme with GeI_4 . Bis(trifluoromethyl)cadmium-glyme (0.901 g (2.65 mmol)) was added in one portion to GeI_4 (0.401 g (0.690 mmol)) in 1,2-dibromoethane (5 mL). The addition of the cadmium reagent resulted in the immediate evolution of volatile materials, the majority of which were produced within 15 min of the addition of the trifluoromethylating agent. Typically, however, the reaction was allowed to proceed for approximately 1 h or until the color of GeI_4 was discharged. During this period the vessel was periodically vented to the vacuum system. After separation, $(\text{CF}_3)_4\text{Ge}$ (0.104 g (0.298 mmol)) and $(\text{CF}_3)_3\text{GeI}$ (0.013 g (0.032 mmol)), were found among the volatile materials recovered; see Table II. The yields of the (trifluoromethyl)germanes, on the basis of GeI_4 , were 43% for $(\text{CF}_3)_4\text{Ge}$ and 4.7% for $(\text{CF}_3)_3\text{GeI}$. Glyme was also recovered from the reaction products.

After the volatile trifluoromethylated germanes had been recovered, the residual solvent in the flask was removed and $\text{Cd}(\text{CH}_3)_2$ (0.7 g) was condensed onto the solid material remaining. From the ensuing reaction $(\text{CF}_3)_3\text{GeCH}_3$ (0.60 g (0.203 mmol)) was separated in 29.5% yield; see Table II.

In another experiment GeI_4 (0.496 g (0.853 mmol)) was added over a 30-min period to $(\text{CF}_3)_2\text{Cd}$ -glyme (0.709 g (2.08 mmol)) in 5 mL of 1,4-dibromobutane. Volatile products were removed as formed, but tetrakis(trifluoromethyl)germane (0.143 g, 42.3% yield) was the only trifluoromethyl-containing germane isolated.

In order to begin to delineate the chemical differences between the various $(\text{CF}_3)_2\text{Cd}$ -base species, the reaction of several other adducts of $(\text{CF}_3)_2\text{Cd}$ with GeI_4 was also assessed. The results of these preliminary reactions are collected in Table III and there compared to the reaction of $(\text{CF}_3)_2\text{Hg}$.

In a control experiment, small aliquots of all of the trifluoromethyl-substituted germanium iodides were combined and sealed into an NMR tube along with excess diglyme. Periodic monitoring of the sample by ^{19}F NMR indicated no reaction over a 3-day period.

Reaction of $(\text{CF}_3)_2\text{Cd}$ -Glyme with PI_3 . Bis(trifluoromethyl)cadmium-

Table III. Reaction of GeI₄ with Trifluoromethyl Group 2B Compounds

reagent ^c	condtns		solvent	product yield, ^a %	
	time, h	temp, °C		(CF ₃) ₂ Ge	other major products
(CF ₃) ₂ Hg ⁹	120	120		15	(CF ₃) ₃ GeF, 11
(CF ₃) ₂ Cd·py	1	23	py	0	0
(CF ₃) ₂ Cd·dg	0.5	23	dg	0	"oxide", ^b 63; (CF ₃) ₂ GeI ₂ , 25
(CF ₃) ₂ Cd·g	1	23	ether	0	(CF ₃) ₂ GeI ₂ , 27
(CF ₃) ₂ Cd·dg	1	23	Br(CH ₂) ₃ Br	0	
(CF ₃) ₂ Cd·g	1	23	CH ₂ Cl ₂	43	"oxide", 30; (CF ₃) ₃ GeI, 5

^a For product characterization see Table II. ^b The compound(s) referred to as "oxide" is involatile in a vacuum line but reacts with Cd(CH₃)₂ to form (CF₃)₃GeCH₃ in, e.g., 63% yield on the basis of the amount of GeI₄ originally taken. The fluorine NMR of the "oxide" contains a singlet at -20.1 ppm vs. CF₃COOH; the chemical shift of (CF₃)₃GeOGe(CF₃)₃ is -21.0 ppm.⁹ The mass spectrum of the "oxide" contains (CF₃)₃GeOCH₂⁺ ions. Methyl iodide is also formed in the ligand-exchange reaction. ^c py = pyridine; dg = diglyme; g = glyme.

-glyme (1.320 g (3.86 mmol)) was slowly added to a solution formed from PI₃ (0.851 g (2.06 mmol)) and 5 mL of 1,6-dibromohexane. Any volatile materials that were formed during the reaction were continuously removed from the vessel during the 30 min required for the addition of the reagent and the discharge of the red coloration due to PI₃. Tris(trifluoromethyl)phosphine and (CF₃)₂PI were recovered in yields that varied widely but occasionally approached 20 and 30%, respectively. The reaction of this group 5A trihalide, which is under further study, appears to be different in nature than the reaction of the group 4A species. For example, one major product is an unstable red material that is maintained in a trap held at -45 °C. This species continually decomposes at ambient temperature evolving PF₃, CF₃I, and glyme. Mass spectra of the red liquid contain dominant CF₃I and PF₃ ions.

Upon reaction of the pyridine or THF adducts of (CF₃)₂Cd with PI₃ in a manner similar to that indicated above, only PF₃ and CF₃I are recovered. The isolated yield of PF₃ from the reaction of the pyridine adduct with PI₃, for example, was 69%, on the basis of the amount of PI₃ taken; in another reaction the yield of CF₃I from (CF₃)₂Cd·(THF)₂ with PI₃ was 85%. The reaction of AsI₃, although less studied, appears similar; (trifluoromethyl)arsines are formed but in relatively low yield.

Reactions of (CF₃)₂M (M = Cd, Hg) with Acyl Halides. Reaction of (CF₃)₂Cd·Glyme with Benzoyl Chloride. At 23 °C (CF₃)₂Cd·glyme (0.590 g, (1.73 mmol)) was quickly added to a well-stirred solution containing benzoyl chloride (0.380 g (2.71 mmol)) in methylene chloride (5 mL). Immediately upon combination the slow evolution of gaseous material from the solution was observed. After cessation of the reaction, approximately 20 min, all volatile materials were removed from the yellow solids which are also formed and separated. Benzoyl fluoride, C₆H₅C(O)F (0.279 g (2.33 mmol)), was recovered from the fraction that had been retained at -45 °C in 86% yield, on the basis of benzoyl chloride. Tetrafluoroethylene was recovered in 40% yield; see Table II.

Benzoyl chloride, tetramethylethylene, and (CF₃)₂Cd·glyme were sealed into an NMR tube in approximately stoichiometric amounts, and the course of the reaction was monitored by ¹⁹F NMR. Over a period of 5 min the characteristic resonances (Table II) of benzoyl fluoride and the difluorocarbene adduct of tetrafluoroethylene, 1,1-difluorotetramethylcyclopropane, were found to appear in the spectrum and to increase in intensity.

Reaction of (CF₃)₂Cd·Glyme with Acetyl Bromide. Over a 5-min interval solid bis(trifluoromethyl)cadmium-glyme (0.663 g (1.94 mmol)) was added to a well-stirred solution of CH₃C(O)Br (0.258 g (2.10 mmol)) in 1,2-dibromoethane (5 mL). The very vigorous production of volatile material was observed upon the addition of the cadmium complex. During the addition, the reaction vessel, at ambient temperature throughout, was periodically vented to the vacuum system; later all volatile materials were removed and separated by fractional condensation. Acetyl fluoride (0.117 g (1.89 mmol)), was retained in a trap maintained at -121 °C. The yield of CH₃C(O)F, based upon the amount of CH₃C(O)Br used, was 90%. Tetrafluoroethylene, separated in 64% yield, was found in a trap maintained at -196 °C. Glyme was retained in a trap held at -78 °C. See Table II.

In a second reaction (CF₃)₂Cd·glyme (0.921 g (2.69 mmol)) was added over a 15-min period to a solution comprised of CH₃C(O)Br (0.903 g (7.34 mmol)) and tetramethylethylene (0.599 g (7.13 mmol)). The reactor was held at -27 °C throughout the experiment. During the addition of the (trifluoromethyl)cadmium reagent, the solution turned a yellow color. After a total of 30 min all volatile materials were removed to the vacuum line from the reactor, which was maintained at -27 °C, and separated.

1,1-Difluoro-2,2,3,3-tetramethylcyclopropane (0.503 g (3.75 mmol)), CH₃C(O)F (0.319 g (5.15 mmol)), and 0.0596 g of unchanged tetramethylethylene were recovered; the yields of the cyclopropane and the acyl fluoride, on the basis of the amount of the cadmium reagent used and with the assumption that it is difunctional, were 69.7 and 96%,

respectively. Tetrafluoroethylene was not recovered.

In a third reaction, which required 40 min, small portions of (CF₃)₂Cd·glyme (0.751 g (2.20 mmol)) were slowly added to a solution containing CH₃C(O)Br (0.631 g (5.13 mmol)), and tetramethylethylene (0.414 g (4.90 mmol)), which had been cooled to -78 °C. Upon addition of the cadmium-containing reagent, a mild effervescing of the solution was observed. As the reaction progressed, a yellow solid precipitated. In order to facilitate mixing, the CO₂/C₂H₅OH bath was removed for approximately 3 min and, as the contents of the flask began to liquify, vigorous production of volatile material was apparent.

The flask was vented to the vacuum system and then recooled to -78 °C. This procedure was repeated several times during the reaction; then the flask was allowed to warm while all volatile materials were removed from the yellow-orange solid remaining and separated into CH₃C(O)F (0.259 g (4.18 mmol)), 95%, on the basis of the cadmium reagent, and the tetramethylethylene adduct C₇H₁₂F₂ (0.316 g (2.36 mmol)), 54%. Tetrafluoroethylene was not observed.

Over a 15-min period bis(trifluoromethyl)cadmium-glyme (0.798 g, (2.35 mmol)) was added to a solution containing 0.502 g (4.08 mmol) of CH₃C(O)Br and 2.61 g (4.66 mmol) of *cis*-2-butene. Throughout the reaction period the contents of the vessel were maintained at -30 °C. After 45 min all material volatile at -30 °C was removed from the then red solution. Acetyl fluoride (0.218 g (3.52 mmol)) and *cis*-2,3-dimethyl-1,1-difluorocyclopropane (0.0692 g (0.653 mmol)) were recovered and identified (Table II). The yields of the fluoride and cyclopropane, on the basis of CH₃C(O)Br originally taken, were 86.3 and 16%, respectively. Small amounts of tetrafluoroethylene (ca. 5% yield) were also isolated. The *trans* isomer of the dimethylethylene adduct, *trans*-2,3-dimethyl-1,1-difluorocyclopropane, was not observed.

The reaction of (CF₃)₂Cd·glyme with acetyl bromide in the presence of *trans*-2-butene was assessed by a reaction similar to that above. The *trans*-cyclopropane isomer was recovered in fairly low yield; no *cis* isomer was observed. See Table II.

Reaction of (CF₃)₂Hg with Benzoyl Chloride. Bis(trifluoromethyl)mercury (0.158 mmol) and an excess of C₆H₅C(O)Cl (1.44 mmol) were sealed into a 4-mm tube under vacuum, and any ensuing reaction was monitored by fluorine NMR. After 1 h at 23 °C no reaction was observed. After 19 h at 120 °C, 37% of the (CF₃)₂Hg had reacted, forming C₆H₅C(O)F and, in part, CF₃HgCl (δ -46.6 ($J_{\text{Hg-F}} = 1867$ Hz), lit.⁴ δ (in benzene) -45.8 ($J_{\text{Hg-F}} = 1869$ Hz)), along with perfluoroalkene. Bis(trifluoromethyl)mercury, when exposed to CH₃C(O)Br, GeI₄, or C₆H₅C(O)Cl in the presence of diglyme, was recovered unchanged after 40 min at ambient temperature.

Results and Discussion

Preparation of the Trifluoromethyl Group 2B Reagents. The synthesis of each of the various Lewis base adducts of (CF₃)₂Cd reported above proceeds easily and cleanly when the base of interest is utilized as the solvent for the reaction. The formation of (CF₃)₂Cd appears to result from the establishment of an equilibrium between all possible (trifluoromethyl)- and methylmercury and methyl- and (trifluoromethyl)cadmium compounds, an equilibrium which is relatively rapidly attained, requiring from only a few minutes for the more basic solvents to about 1 day for THF (Figure 2). Lewis base exchange of the cadmium coordinated bases, e.g., pyridine for glyme, a type of reaction that might be required for the preparation of compounds containing Lewis bases that have high melting points, proceeds readily. Once isolated the (trifluoromethyl)cadmium complexes are typically fairly stable thermally with the adducts of stronger bases being the least affected by exposure to ambient temperatures. The glyme complex of (CF₃)₂Cd, for example, decomposes at a rate of about

Table IV. Formation of (Trifluoromethyl)stannanes: Comparison of Techniques

method	reaction	(CF ₃) ₄ Sn yield, %	amount
radio freq discharge	·CF ₃ + SnI ₄ ⁴	90	1 g/24 h ⁵
CF ₃ radicals + Sn atoms	·CF ₃ + Sn(^g) ₆	0.8	small
divalent Sn	CF ₃ I + SnI ₂ ⁶	0	
low temp fluorination	F ₂ /He + Sn(CH ₃) ₄ ¹¹	0	
ligand exchange with mercurial	(CF ₃) ₂ Hg + SnBr ₄ ^{8,10}	0	
ligand exchange with mercurial	(CF ₃) ₂ Hg + Sn(CH ₃) ₄ ¹⁸	0	
ligand exchange with cadmium	(CF ₃) ₂ Cd·g + SnI ₄	66	unlimited

5% per day at ca. 23 °C, a rate compatible with the yields indicated in Table I. The diglyme complex appears to be stable for weeks under the same conditions.

The purification procedures reported here rely upon the observation that (CF₃)₂Cd forms stronger Lewis base adducts than do the mercurials or Cd(CH₃)₂. Under vacuum the less stable adducts dissociate, yielding volatile materials which are then removed from the vessel leaving a white, or for pyridine light cream colored, powder which, by hydrolysis, is typically ca. 95% pure. Further purification by recrystallization is possible, but the material is most often used as obtained. The relatively high yields of isolated material are an indication that under vacuum the hydrogen rich organometallic species are preferentially removed from the reactor resulting in a larger amount of (CF₃)₂Cd·L separated than is present at equilibrium; see Figure 2. The yields appear to be functions of the base present, ranging from 40 to 50% for THF to 70% for diglyme. During the preparation very little, if any, decomposition of the organometallic species is observed. As yet, bis(trifluoromethyl)cadmium uncomplexed by base has not been isolated.

Reactions of Inorganic Halides. The reactivity of three representative main-group halides, SnI₄, GeI₄, and PI₃, toward (CF₃)₂Cd·L was assessed for several reasons. One consideration was to determine if these reactions might result in the formation of fully substituted trifluoromethyl organometallics in good yield under readily attainable conditions, i.e., without requiring the purchase or construction of experimental apparatus not available in most laboratories. In order to help compare the present results to those of previously reported syntheses, the experimental methods and the yields of one example, tetrakis(trifluoromethyl)tin, attained both here and from other attempted trifluoromethyltin preparations have been collected in Table IV.

Clearly, the only viable alternative preparation for (CF₃)₄Sn is the radio frequency discharge of C₂F₆ which generates CF₃ radicals that then react with SnI₄. Aside from the limited availability of the required apparatus the disadvantages of that procedure are first that the product must be separated from the fluorocarbons which are simultaneously formed in the discharge, a process that can be laborious, and second that the conversion occurs at a rate, 1 g/24 h⁵, which is relatively low, especially when compared to the amounts that can now be prepared by ligand exchange. The previously reported reactions between (CF₃)₂Hg and either SnBr₄ or Sn(CH₃)₄ do not result in the formation of (CF₃)₄Sn because at the temperatures required to provide the activation energy for ligand exchange, (CF₃)₄Sn is unstable.^{9,18} Since the (fluoroalkyl)cadmium reagent is active at temperatures 100 °C below those required for ligand exchange with mercury, thermal decomposition of the (trifluoromethyl)stannanes produced here is not observed.

The fully substituted germane, (CF₃)₄Ge, has been found to be much more thermally stable than (CF₃)₄Sn,⁹ and the former species has been prepared by a number of methods including ligand-exchange reactions between GeBr₄ or GeI₄ and (CF₃)₂Hg. However, that reaction requires 120 h at 120 °C, and the max-

imum yield (22%) is obtained only in the presence of substoichiometric amounts of the mercurial. As the amounts of (CF₃)₂Hg utilized approach a 2:1 molar ratio, the yield of (CF₃)₄Ge declines, presumably due to the acid-catalyzed decomposition of tetrakis(trifluoromethyl)germane.⁹

In the present study germanium tetraiodide was selected as a substrate first to determine if germanium halides were also reactive at ambient temperature and second to examine the effect, if any, of variation in solvent or Lewis base affixed to cadmium. As shown in Table III the course of the reaction is markedly affected by the nature of the base used. Although all of the cadmium-containing reagents are reactive at room temperature, the glyme adduct is the most efficient for the preparation of (CF₃)₄Ge. When compared to the mercurial (Table III), the reaction of (CF₃)₂Cd·glyme with GeI₄ is seen to require only about 1% of the time yet twice the amount of (CF₃)₄Ge is formed.

If, however, trisubstituted species of the type (CF₃)₃GeR are the desired product, the diglyme adduct of (CF₃)₂Cd is the preferred reagent. Mass spectral and NMR evidence (Table III) indicate that the reaction of (CF₃)₂Cd·diglyme with GeI₄ results in the formation of tris(trifluoromethyl)germanium alkoxides which have been shown to be chemically reactive by the formation of (CF₃)₃GeCH₃ in 63% overall yield after the addition of dimethylcadmium to the tris(trifluoromethyl)germanium "oxide". Presumably, the formation of other derivatives of the (CF₃)₃Ge moiety could be accomplished by the introduction of the requisite reagent to the "oxide" in a manner similar to that previously demonstrated for (CF₃)₃GeI.⁷ Further studies designed to clarify the role of the Lewis base in the ligand-exchange reaction and to ascertain the identity and the method of formation of the oxide linkage to the tris(trifluoromethyl)germanium group are in progress.

Currently (trifluoromethyl)phosphines are typically formed by the interaction of elemental phosphorus with CF₃I at elevated temperatures and pressures as originally described by Emeleus.³ Although this method is both laborious and tedious, at present other, more convenient, large scale preparations are unknown. Ligand-exchange reactions of PI₃ with (CF₃)₂Cd·base, while extremely convenient for the synthesis of small amounts of (CF₃)₃P, have not, as yet, proven to be capable of supplanting the traditional reaction when larger amounts of material are desirable.

The nature of the reaction of PI₃, a Lewis base, with (CF₃)₂Cd·base appears to differ significantly from that of either GeI₄ or SnI₄, both Lewis acids. Although all the (trifluoromethyl)germanium iodides have been shown to be stable toward the Lewis base diglyme in the absence of cadmium compounds, clearly during the ligand-exchange process itself the germanes as then present interact with diglyme, possibly still complexed, to generate CH₃I and the species presently formulated as (CF₃)₃GeOR. Tetrafluoroethylene is frequently found as a by-product of the reaction but CF₃I or the metal fluorides have not, as yet, been observed.

During the reaction of the group 5A halide, however, neither C₂F₄ nor CH₃I are isolated, and the major products of the side reactions associated with this ligand exchange are PF₃ and CF₃I. Although both exchange reactions are under further study, one currently tenable possibility is that in the case of Lewis base substrates, like the phosphines, (CF₃)_nPI_{3-n}, one step of the reaction pathway is the displacement of the original base ligand, e.g., glyme or diglyme, from cadmium with the concomitant formation of a phosphorus-cadmium adduct, a step somewhat akin to the Lewis base exchange reactions described above. Seemingly, this (red) adduct then decomposes to eventually yield CF₃I and PF₃. For the group 4A halides and the trifluoromethylated species derived therefrom, the formation of a similar type of cadmium adduct is not indicated.

Of the solvent systems examined in a cursory fashion during the present study, haloalkanes appear to be the solvents of choice for ligand-exchange reactions as they are unreactive with both products and reagents. A further advantage is that by means of judicious choice of solvent volatility, separation procedures may be greatly simplified.

Reactions with Acyl Halides. The original impetus for the study of the reactions of $(CF_3)_2Cd$ -glyme with acyl halides was a desire to compare the reactivity of a perfluoroalkyl organometallic species to that of its perhydrogenated derivative. Dialkylcadmium compounds are, of course, well-known reagents for the conversion of acyl halides to ketones. The reaction utilizing alkylcadmium reagents occurs in fair to good yields, especially if catalyzed by inorganic lithium or magnesium salts.¹⁹ In the present case inorganic salts were not added in order to determine the inherent reactivity of the parent perfluorinated organometallic species, as isolated. The reaction of the (perfluoroalkyl)cadmium reagents in the presence of added salts is currently under study.

When in excess, the acyl halides examined reacted smoothly and essentially completely with $(CF_3)_2Cd$ -glyme to yield 2 mol of the acyl fluorides and near 70% of the calculated amount of CF_2 . The latter can be isolated either as the dimer, C_2F_4 , or as the difluorocarbene adduct of, e.g., tetramethylethylene, 1,1- F_2 -(CH_3)₄- C_3 . With acetyl bromide the reaction proceeds at temperatures at least as low as $-78^\circ C$ although at that temperature the solution employed begins to freeze as the cyclopropane is formed. The minimum temperature for the reaction is currently unknown.

If the interaction of the acyl halide and the (perfluoromethyl)cadmium compound occurs in the presence of *cis*-2-butene, the only cyclopropane isolated is *cis*-1,1-difluoro-2,3-dimethylcyclopropane. If in the presence of *trans*-2-butene, only the *trans* isomer of the cyclopropane is observed. Although the yields of the dimethylcyclopropanes, at the temperatures reported, are modest, these reactions do indicate that the addition of CF_2 to the ethylene linkages is stereospecific, which in turn implies that the difluorocarbene (oid) is present in the singlet state. The reduction in the yields of the cyclopropane which are found when the substrate is dimethylethylene rather than tetramethylethylene can be attributed, in part, to the electrophilic nature of the CF_2 intermediate.

This difluorocarbene-transfer reaction occurs at a much lower temperature and in much less time than is required for conventional chemical synthesis of the CF_2 group. Typically, the formation of difluorocarbene from organometallic precursors, like $CF_3HgC_6H_5$, requires prolonged heating at temperatures of at least $85^\circ C$ even in the presence of diglyme and metal halides.²⁰ For organic precursors, like $ClCF_2CO_2^-$, temperatures of $140^\circ C$

are typically utilized.²¹ Although mechanistic studies are still in progress, it is abundantly clear that operationally the (perfluoroalkyl)cadmium-acyl halide reaction generates difluorocarbene at very low temperatures and that this system could be of considerable importance for the synthesis of fluorinated organic and inorganic species too unstable to survive the harsher thermal conditions previously required. Finally, it should be noted that the present reaction is the mildest, gentlest synthesis of acyl fluorides yet known.²²

Conclusion

The various $(CF_3)_2Cd \cdot L_n$ (L = Lewis base) species that have been examined are easily and conveniently prepared by ligand-exchange reactions between dimethylcadmium and bis(trifluoromethyl)mercury. The yields of the (trifluoromethyl)cadmium reagents are good, ranging from 40 to 70%; purification is trivial. Once formed the reagents are very reactive and three types of interactions have been investigated. The first is base exchange which is shown to occur readily upon dissolving the bis(trifluoromethyl)cadmium-glyme adduct in, e.g., dimethyltellurium. The second series of reactions demonstrate the relatively gentle conditions required to form trifluoromethyl derivatives of representative main-group elements, like $(CF_3)_4Ge$, $(CF_3)_4Sn$, or $(CF_3)_3P$, all of which can be formed within minutes at ambient temperatures; previous syntheses which utilized $(CF_3)_2Hg$ typically required several days at temperatures of ca. $120^\circ C$ or failed entirely. The third category of substrate, acyl halides, reacts smoothly and completely at subambient temperatures to generate the corresponding acyl fluorides in excellent yield. The formation of difluorocarbenes in the presence of the acyl halides is demonstrated by stereospecific trapping reactions with alkenes. Again the (trifluoromethyl)cadmium reagent is shown to be a much better reagent than $(CF_3)_2Hg$ since the reaction of benzoyl chloride occurs rapidly at $23^\circ C$ with cadmium whereas the corresponding reaction requires 19 h at $120^\circ C$ for the mercurial, even then 63% of the $(CF_3)_2Hg$ remains.

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(19) We thank Professor Dennis Tuck, Department of Chemistry, University of Windsor, for sharing his knowledge of cadmium chemistry with us. See, for example, J. Kollonitsch, *Nature (London)*, **188**, 140 (1960).

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