Perfluoroisopropylcadmium and copper: preparation, stability and reactivity

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Abstract

Perfluoroisopropylcadmium can be prepared in excellent yield (98%) from $(CF_3)_2CFI$ and activated cadmium powder in DMF at room temperature under degassed conditions. The resultant cadmium reagent undergoes metathesis with copper(I) salts to give perfluoroisopropylcopper, in quantitative yield. While perfluoroisopropylcopper is stable in DMF at room temperature under nitrogen, the cadmium counterpart decomposes to a mixture of dimers and trimers of hexafluoropropene, under the same conditions. Sulfur dioxide can be inserted into the cadmium–carbon bond in perfluoroisopropylcadmium while no reaction was observed with the corresponding copper reagent. No stable F-alkylcadmium could be obtained from the reaction of $CF_3CF_2CFICF_3$ with either Cd powder or Me_2Cd; only the elimination product, $CF_3CF=CFCF_3$, was observed. Perfluoroalkylation reactions with F-isopropylcadmium/copper in DMF met with limited success.

Introduction

Although many linear-chain perfluoroalkyl organometallic compounds are known, relatively little has been reported on branched chain F-alkyl organometallics. The first F-isopropyl organometallic compounds reported were $(CF_3)_2CFLi$, $(CF_3)_2CFMgBr$ and $(CF_3)_2CFZnI \cdot dioxan$ [1]. $(CF_3)_2CFLi$ and $(CF_3)_2CFMgBr$ were prepared via exchange reaction between $(CF_3)_2CFI$ and alkyllithium or Grignard reagents, respectively, at low temperature. The $(CF_3)_2CFZnI \cdot dioxan$ was obtained by refluxing F-isopropyl iodide with zinc dust in dioxan. Later, $[(CF_3)_2CF]_2Hg$ [2, 3] and $(CF_3)_2CFAg \cdot CH_3CN$ [4] were synthesized from $CF_3CF=CF_2$ and the corresponding metal fluoride. Alternatively, metal atom reactions at -196 °C afforded silver and zinc complexes, $(CF_3)_2CFAg$ and $(CF_3)_2CFZnI$, albeit in low yields [5]. More recently, $[(CF_3)_2CF]_2Cd \cdot 2CH_3CN$ was obtained in quantitative yield from the reaction of dimethylcadmium and $(CF_3)_2CFI$ in acetonitrile [6]. Additionally, the perfluoroisopropylsilver complexes, $(CF_3)_2CFAg \cdot CH_3CN$ and $[(CF_3)_2CF]_2Ag^-$, have been characterized by X-ray crystallography [7].

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We have reported facile preparations of a number of stable F-alkyl [8, 9], aryl [8, 10], alkenyl [11–13], alkynyl [14], allyl [15] and difluoromethylcadmium [16] reagents by treatment of the appropriate fluorinated iodide or bromide with acid-washed cadmium powder in DMF at room temperature. Metathesis of these cadmium reagents with copper(I) salts gave the corresponding copper reagents [10, 14–20]. The objectives of this study were: (a) to determine whether a secondary F-alkylcadmium reagent could be prepared by the above method; (b) to examine the thermal stability and chemical reactivity of the cadmium reagent; and (c) to examine possible metathesis with copper(I) halides as a route to the corresponding F-secondary copper reagent.

Experimental

General

All NMR spectra were recorded on a JEOL FX90Q or Bruker AC 300 spectrometer. ^{19}F NMR chemical shifts are reported in ppm relative to CFCl$_3$ as internal standard, ^{1}H NMR spectra were referenced to internal TMS with chemical shifts again reported in ppm. The GC–MS spectra were acquired from a VG TRIO-1 mass spectrometer, operating at 70 eV.

Dimethylformamide, CH$_3$CN and pyridine were distilled over CaH$_2$, P$_2$O$_5$ and KOH, respectively. Cadmium powder (100 mesh), copper halides, isobutylene and 2-butene were purchased from Aldrich Chemical Co. Cadmium powder was activated by acid wash; CuCl and CuBr were purified by a published procedure [21]. Nonafluoro-2-iodobutane (CF$_3$CF$_2$CFICF$_3$) was prepared from perfluoro-2-butene, KF and I$_2$ as reported by Krespan [22]. Dimethylcadmium was prepared from MeLi and CdBr$_2$ in Et$_2$O, and separated by fractionation at -78 °C. All ^{19}F NMR yield calculations were carried out with the addition of a known quantity of PhCF$_3$ to the sample solution.

Preparation of $(CF_3)_2CFCdX$ $[X = (CF_3)_2CF$ or $I]$

(a) Under degassed conditions

A 100 ml round-bottomed one-necked flask, equipped with a nitrogen tee, septum port and a magnetic stir bar was charged with activated cadmium powder (50 mmol) and 50 ml DMF under a nitrogen purge. The nitrogen tee was then replaced by a vacuum take-off valve with a Teflon stop-cock. With the Teflon valve closed, the flask was attached to a standard vacuum line, the reaction mixture was frozen by liquid nitrogen and evacuated at ca. 0.005 mmHg pressure for 5 min. Then (CF$_3$)$_2$CFI (25 mmol) was condensed into the flask, the Teflon valve closed, the flask was warmed to room temperature and the reaction mixture stirred at that temperature for 10 min. A pale yellow reaction mixture resulted. Fluorine NMR analysis of the supernatant indicated the formation of a mixture of mono- and bis-(perfluoroisopropyl)cadmium (57:43) in 98% yield. ^{19}F NMR δ: -69.7 (d, 6F); -217.6 (hept, 1F) $(^2J(CdF) \sim 110$ Hz, $^3J(CdF) = 36$ Hz, $^3J(FF) = 12$ Hz for

$(CF_3)_2CFCdI$); -70.2 (d, 6F); -217.7 (hept, 1F) ppm ($^2J(CdF) \sim 105$ Hz, $^3J(CdF) = 32$ Hz, $^3J(FF) = 12$ Hz for $[(CF_3)_2CF]_2Cd$).

(b) Under nitrogen

Activated cadmium powder (20 mmol) and DMF (20 ml) were placed in a 50 ml one-necked round-bottomed flask with a septum port equipped with a Dry Ice/isopropanol cooled condenser, magnetic stir-bar and a nitrogen tee. Then $(CF_3)_2CFI$ (10 mmol) was added dropwise via a cooled syringe to a suspension of Cd in DMF, and the reaction mixture stirred for 10 min. An exothermic reaction with subsequent formation of a pale yellow supernatant was observed. ^{19}F NMR analysis of the supernatant indicated the formation of $(CF_3)_2CFCdX$ (mono/bis = 67:33) reagent in 78% yield.

(c) In acetonitrile at 75–78 °C

Under nitrogen [apparatus as described in (b)], a stirred mixture of Cd powder (20 mmol), CH_3CN (20 ml) and $(CF_3)_2CFI$ (10 mmol) was heated to 75–78 °C, and maintained at that temperature for 20 min. A pale yellow reaction mixture resulted. ^{19}F NMR spectral analysis of the supernatant liquid exhibited resonances for $(CF_3)_2CFCdX$ (74% yield). ^{19}F NMR δ: -69.3 (d, 6F); -215.9 (hept, 1F) ($^2J(CdF) = 121$ Hz, $^3J(CdF) = 40$ Hz, $^3J(FF) = 12$ Hz for $(CF_3)_2CFCdI$); -69.7 (d, 6F); -216.6 (hept, 1F) ppm ($^2J(CdF) = 109$ Hz, $^3J(CdF) = 36$ Hz, $^3J(FF) = 12$ Hz for $[(CF_3)_2CF]_2Cd$).

Hydrolysis of $(CF_3)_2CFCdX$ to $(CF_3)_2CFH$

Perfluoroisopropylcadmium was prepared from activated cadmium powder (30 mmol) and 2-iodoperfluorpropane (15 mmol) in 30 ml DMF under degassed condition [as described in (a) above]. The reaction flask was flushed with N_2, then 10 ml water was added dropwise to the stirred cadmium reagent via a syringe. The volatiles were removed under vacuum and fractionally distilled at room temperature. The most volatile product was collected in a liquid N_2 trap, to afford 1.6 g (63%) of $(CF_3)_2CFH$. ^{19}F NMR ($CDCl_3$) δ: -76.6 (dd, 6F); -214.3 (d hept, 1F) ppm ($^2J(FH) = 44$ Hz, $^3J(FH) = 5$ Hz, $^3J(FF) = 12$ Hz). ^1H NMR ($CDCl_3$) δ: 4.90 (d hept) ($^2J(FH) = 44$ Hz, $^3J(FH) = 5$ Hz). GC/MS (m/e, % rel. int.): (no M^+) 151 (96); 131 (3); 112 (0.3); 100 (8); 69 (100); 50 (51).

Addition of Br_2 to $(CF_3)_2CFCdX$

A 50 ml one-necked round-bottomed flask equipped with septum port, magnetic stir-bar and Dry Ice/isopropanol condenser was flushed with and maintained under nitrogen, then 35 ml of a 0.23 M solution of $(CF_3)_2CFCdX$ in DMF was added to the flask via a syringe. The flask was cooled with an ice bath and bromine (10 mmol) was added over a period of 5 min to the stirred solution of the cadmium reagent. After 30 min, ^{19}F NMR analysis indicated the formation of $(CF_3)_2CFBr$ (78%) ^{19}F NMR δ: -74.8 (d, 6F); -156.8 (hept, 1F) ppm ($^3J(FF) = 15$ Hz). GC/MS (m/e, % rel. abund.): 248/250 (M^+, 27); 231/229 (10); 169 (21); 131 (14); 100 (16); 69 (100).

Stability of (CF₃)₂CFCdX in DMF

(a) At room temperature

A 1.0 ml aliquot of a 0.32 M of $(CF_3)_2CFCdX$ in DMF was transferred to an NMR tube equipped with a Young valve, degassed and maintained at room temperature. A gradual reduction in the intensities of the resonances due to the cadmium reagent was observed by ^{19}F NMR analysis. After 8 h at room temperature, the reaction mixture became cloudy with the formation of a colorless layer at the bottom of the tube and no $(CF_3)_2CFCdX$ remained in the solution (multiple resonances between -59 to -200 ppm were observed in the ^{19}F NMR spectrum).

(b) At 60 °C

In the same manner, a 1.0 ml aliquot of 0.32 M $(CF_3)_2CFCdX$ in DMF was prepared in an NMR tube under degassed conditions. This tube was heated in an oil bath at 60 °C for 30 min; at the end of this period the reaction mixture became cloudy with a colorless layer at the bottom of the tube. ^{19}F NMR analysis of the solution indicated the absence of $(CF_3)_2CFCdX$.

Decomposition of (CF₃)₂CFCdX in the presence of Z-CH₃CH=CHCH₃/ (CH₃)₂C=CH₂ in DMF

Into a solution of $(CF_3)_2CFCdX$ (prepared from 3 mmol $(CF_3)_2CFI$ and 6 mmol Cd in 1.5 ml DMF under degassed conditions) in an NMR tube with a Young valve, was condensed 3.5 mmol of Z-CH_3CH=$CHCH_3$. The tube was sealed, brought to room temperature and the contents well mixed. After 20 h at room temperature, no $(CF_3)_2CFCdX$ was observed in the solution by ^{19}F NMR spectroscopy. Resonances attributable to the 1,1-bis-(trifluoromethyl)cyclopropane adduct (E or Z) [23] were not detected in the ^{19}F NMR spectrum of the reaction mixture. Only the formation of the colorless bottom layer was observed. Similarly, decomposition of the cadmium reagent was carried out in the presence of $(CH_3)_2C$=CH_2. Again, only the formation of a colorless fluorocarbon bottom layer was observed with no 1,1-bis(trifluoromethyl)cyclopropane adduct [23].

Decomposition of (CF₃)₂CFCdX in DMF

Into a 100 ml one-necked round-bottomed flask with a septum port, magnetic stir-bar and a nitrogen tee was introduced 45 ml of a 0.49 M $(CF_3)_2CFCdX$/DMF solution. This solution was stirred at room temperature for 18 h under nitrogen. A colorless layer settled at the bottom of the flask which was separated with a syringe. Distillation of this layer at room temperature (0.01 mmHg) gave a 2.4 g of a colorless liquid. GLPC analysis of this material indicated six compounds. Separation via preparative GLPC afforded two major and one minor fractions. The mass spectra of the two major fractions contained molecular ions and all expected fragments for HFP dimers and trimers. GC/MS (*m/e*, % rel. int.): 300 (M⁺, 69); 281 (58); 231 (45); 212 (20); 193 (11); 181 (100); 150 (40); 131 (33); 69 (26) for dimers of HFP, and 450 (M⁺, 0.2); 431 (17); 381 (4); 362 (8); 343 (15); 293

(24); 281 (13); 243 (22); 231 (9); 181 (57); 169 (3); 150 (10); 131 (11); 119 (36); 100 (10); 69 (100) for trimers of HFP.

Metathesis of $(CF_3)_2CFCdX$ to $(CF_3)_2CFCu$ in DMF

   (a) In a 2:1 molar ratio

   At room temperature, 10 ml of a 0.32 M solution of $(CF_3)_2CFCdX$ in DMF was added to 6.48 mmol of CuCl in a 50 ml one-necked round-bottomed flask equipped with septum port, a magnetic stir-bar and a nitrogen tee. The reaction mixture was stirred for 2 h at room temperature; a cloudy reaction mixture of two perfluoroisopropylcopper species in quantitative yield was formed. In the same way, metathesis between 2 equiv. of each copper(I) salt (CuBr/CuI/CuCN) and 1 equiv. of the cadmium reagent was carried out. The percentages of the two types of copper reagent are given in Table 1. ^{19}F NMR δ: -68.6 (d, 6F); -213.1 (hept, 1F) ppm (^3J(FF))$= 12$ Hz for $(CF_3)_2CFCu$); -68.6 (d, 6F); -217.5 (hept, 1F) ppm (^3J(FF))$= 12$ Hz for $[(CF_3)_2CF]_2Cu^-$) in the case of CuCN: -68.8 (d, 6F); -215.9 (hept, 1F) (^3J(FF))$= 12$ Hz); -68.6 (d, 6F); -217.5 (hept, 1F) (^3J(FF))$= 12$ Hz for $(CF_3)_2CFCu$ and $[(CF_3)_2CF]_2Cu^-$, respectively).

   (b) In a 1:1 molar ratio

   These reactions were carried out as described above except that 1 equiv. of the reactants was employed. Distribution of the two types of copper reagent is given in Table 1.

Stability of $(CF_3)_2CFCu$ and $[(CF_3)_2CF]_2Cu^-$ in DMF

   A 0.21 M solution of $(CF_3)_2CFCu$ in DMF [prepared from 2 equiv. CuCl and 1 equiv. $(CF_3)_2CFCdX$] was heated in an oil bath at 60 °C. The decomposition of the copper reagent was monitored by ^{19}F NMR analysis. After 30 min, 85% of the original $(CF_3)_2CFCu$ remained in the solution. The temperature was raised to 80 °C and after 1.75 h 75% remained; after 1 h at 90 °C only 25% of the original $(CF_3)_2CFCu$ reagent remained. In the same

TABLE 1

Metathesis of perfluoroisopropylcadmium with copper(I) salts in DMF

CuX	CuX/$(CF_3)_2CFCdX$ ratio	$(CF_3)_2CFCu$ yield (%)[a]	$[(CF_3)_2CF]_2Cu^-$ yield (%)[a]
CuCl	2:1	77	23
CuBr	2:1	54	46
CuI	2:1	12	88
CuCN	2:1	53	47
CuCl	1:1	66	34
CuBr	1:1	40	60
CuI	1:1		100
CuCN	1:1	23	77

[a]Determined by integration of the $>$CFCu signal in the ^{19}F NMR spectra.

manner, a 0.19 M solution of $([CF_3]_2CF]_2Cu^-$ was heated. In this case only 22% of the original copper reagent was left in the solution after 1.75 h at 80 °C. Complete decomposition occurred on heating at 90 °C for 1 h.

Insertion of SO_2 into $(CF_3)_2CFCdX$, $(CF_3)_2CFCu$ and $[(CF_3)_2CF]_2Cu^-$

(a) Into a 50 ml round-bottomed flask with a septum port, nitrogen tee, a magnetic stir-bar and a Dry Ice/isopropyl alcohol condenser was introduced 20 ml of a 0.39 M solution of $(CF_3)_2CFCdX$ in DMF. The flask was cooled with an ice bath. To the stirred solution of the cadmium reagent was condensed excess (~ 15 mmol) sulfur dioxide via the Dry Ice/isopropanol condenser. An immediate exotherm ensued. The reaction mixture was stirred for another 30 min. ^{19}F NMR analysis indicated the complete disappearance of the cadmium reagent with the formation of new resonances at -68.1 (d, 6F); -186.0 (hept, 1F) ppm ($^3J(FF) = 10$ Hz for the SO_2 inserted product).

(b) As described above, 15 ml of a 0.18 M solution of $(CF_3)_2CFCu$ in DMF was allowed to react with excess SO_2. No new resonances were observed in the ^{19}F NMR spectrum; only the starting material was found even after stirring for 6 h. The same result was observed when the reaction was carried out with $[(CF_3)_2CF]_2Cu^-$ and SO_2 in DMF.

Reaction of $CF_3CF_2CFICF_3$ with Cd/Me_2Cd

(a) Into an NMR tube equipped with a Young valve were introduced activated Cd (3.0 mmol) and 1.5 ml DMF under nitrogen. The tube was attached to a standard vacuum line, degassed and $CF_3CF_2CFICF_3$ (1.5 mmol) condensed into the tube. Then the Young valve was closed and the tube warmed to room temperature. A vigorous exotherm resulted with subsequent formation of a pale yellow supernatant. ^{19}F NMR analysis indicated major resonances at -69.1 (m, 6F); -160.4 (m, 2F) ppm for E-$CF_3CF=CFCF_3$, and at -66.8 (m, 6F); -144.0 (m, 2F) ppm for Z-$CF_3CF=CFCF_3$ ($E/Z = \sim 3/1$)*.

(b) In a similar manner, a degassed mixture of Me_2Cd (2.0 mmol), $CF_3CF_2CFICF_3$ (4.0 mmol) and CH_3CN (1.0 ml) was allowed to react from -196 °C to room temperature. A vigorous reaction with gaseous evolution was observed. The ^{19}F NMR spectrum of the reaction mixture at room temperature exhibited resonances for $CF_3CF=CFCF_3$ ($E/Z = \sim 3/1$) only.

Reaction of $(CF_3)_2CFCdX$ with PhI and with $BrCH_2CH=CH_2$

Into a 10 ml flask with a septum port, nitrogen tee and stir-bar was introduced 4 ml of a 0.33 M DMF solution of $(CF_3)_2CFCdX$. To this solution, 1.5 mmol of PhI was added and the reaction mixture stirred at room temperature. After 15 h ^{19}F NMR analysis revealed the complete disappearance of the cadmium reagent with no $PhCF(CF_3)_2$ in the reaction mixture. Similarly, a mixture of 4 ml of a 0.33 M $(CF_3)_2CFCdX$ solution in DMF and 1.5 mmol

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*An authentic sample of perfluoro-2-butenes (E/Z) exhibited the same set of resonances in the ^{19}F NMR spectrum

$BrCH_2CH=CH_2$ was stirred for 15 h at room temperature. ^{19}F NMR analysis showed complete disappearance of the cadmium reagent once more. The expected product, $(CF_3)_2CFCH_2CH=CH_2$, was not detected by ^{19}F NMR or GC/MS analyses of the flash-distilled material.

Reaction of $(CF_3)_2CFCdX$ and PhCOCl with pyridine as the cosolvent

To 15 ml of a 0.46 M DMF solution of $(CF_3)_2CFCdX$ contained in a 25 ml round-bottomed flask equipped with septum port, were added 15 ml pyridine and 8 mmol PhCOCl. This reaction mixture was stirred under nitrogen at 0 °C for 20 min and then at room temperature for 1 h. The products and the solvent were removed under vacuum and poured into conc. HCl; the bottom layer was collected. Distillation at 79–82 °C/40 mmHg {lit. [24] b.p., 80–81 °C/39 mmHg} afforded 0.58 g (30%) $PhCOCF(CF_3)_2$ (GLPC 100%). ^{19}F NMR (CDCl$_3$) δ: − 74.7 (d, 6F); − 179.4 (hept, 1F) ppm $(J(FF))=$ 11 Hz {lit. [24] ^{19}F δ: − 74 and − 177.5 ppm}). ^{1}H NMR (CDCl$_3$) δ: 7.45 (t, 2H, $J(HH)=8$ Hz); 7.62 (t, 1H, $J(HH)=7$ Hz); 7.91 (dm, 2H) ppm. GC/MS (m/e, % rel. int.): 274 (M$^+$, 19); 169 (2); 150 (2); 105 (100); 77 (54); 69 (7).

*Reaction of $(CF_3)_2CFCu$ with PhI and $BrCH_2CH=CH_2$*

Into a 25 ml round-bottomed flask equipped with a septum port, nitrogen tee and a magnetic stir-bar was introduced 10 ml of a 0.35 M solution of $(CF_3)_2CFCu$ in DMF (prepared from CuCl and $(CF_3)_2CFCdX$ in a 2:1 ratio) and 4 mmol of C_6H_5I. This reaction mixture was stirred under N_2 at room temperature for 18 h. ^{19}F NMR analysis of the reaction mixture indicated only the unreacted copper reagent { − 68.6 (d, 6F); − 213.1 (hept, 1F) ppm, $J(FF)=12$ Hz}. The reaction mixture was heated to 80–90 °C for 2 h. The only product detected by ^{19}F NMR analysis was $(CF_3)_2CFH$ with no copper reagent left in the solution.

As described above, a mixture of 4 mmol $BrCH_2CH=CH_2$ and 10 ml of a 0.35 M solution of $(CF_3)_2CFCu$ in DMF was stirred at room temperature for 18 h. The expected product, $(CF_3)_2CFCH_2CH=CH_2$, was not observed in the reaction mixture by ^{19}F NMR analysis.

Results and discussion

A mixture (57:43) of mono- and bis-*F*-alkylcadmium reagents (98%) is obtained when acid-washed cadmium powder is treated with $(CF_3)_2CFI$ in DMF under degassed conditions*.

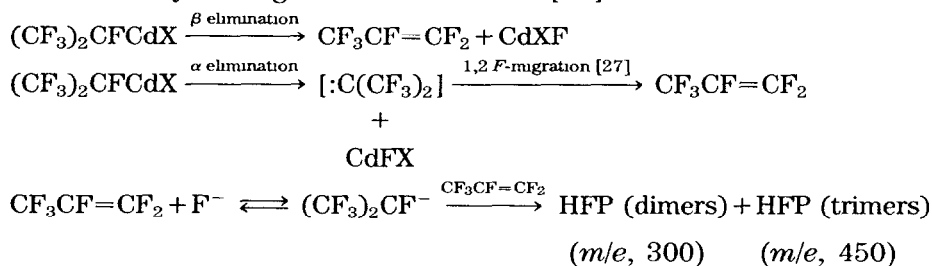$$(CF_3)_2CFI + 2Cd \xrightarrow[-196\,°C\,\rightarrow\,RT]{DMF} (CF_3)_2CFCdI + [(CF_3)_2CF]_2Cd + CdI_2$$

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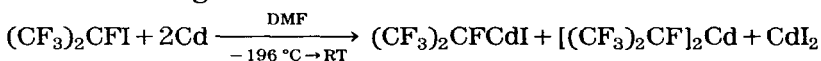
*The exact nature of the aggregation of *F*-isopropyl cadmium/copper complexes in solution is not known; for simplicity they are represented as $(CF_3)_2CFCdX$, $(CF_3)_2CFCu$ and $[(CF_3)_2CF]_2Cu^-$.

When the reaction is carried out under nitrogen the yield of the cadmium reagent was found to be slightly lower (78%). The reaction is exothermic and generally complete in ~ 5 min at room temperature. The ^{19}F NMR spectrum of the mono-cadmium reagent exhibited a doublet at -69.7 (CF_3) and a heptet at -217.6 (CF) ppm, while the bis-reagent resonances were observed at -70.2 (d) and -217.7 (hept) ppm, together with the expected cadmium satellites. The assignment of the mono- and bis-reagent was facilitated by the addition of CdI_2 to a mixture of $(CF_3)_2CFCdX$, which shifted the Schlenk equilibrium toward the mono-reagent. When CH_3CN was employed as the solvent, no cadmium reagent was observed at room temperature. However, after heating the reaction mixture to 70–75 °C for 30 min, a 74% yield of $(CF_3)_2CFCdX$ {X = $(CF_3)_2CF$ or I} (mono/bis = 67:33) resulted. In this reaction, the formation of the coupled product, $(CF_3)_2CF-CF(CF_3)_2$, was not detected by ^{19}F NMR analysis. This observation is in contrast to the reaction of long-chain primary F-alkyliodides reported previously [25]. In the ^{19}F NMR spectrum, the Cd satellites of $(CF_3)_2CFCdX$ in acetonitrile were sharper than in DMF. Hydrolysis of the cadmium reagent afforded $(CF_3)_2CFH$ (63% isolated yield), while treatment with bromine resulted in $(CF_3)_2CFBr$ (78% ^{19}F NMR yield). Reaction with sulfur dioxide gives the corresponding sulfinate in quantitative ^{19}F NMR yield.

Perfluoroisopropylcadmium is unstable in DMF at room temperature under both N_2 and degassed conditions, with concomitant formation of a colorless fluorocarbon bottom layer. Complete decomposition occurred in ~ 8 h at room temperature. Heating accelerates the decomposition (~ 60 °C for 30 min). The fluorocarbon layer could easily be separated via a syringe. After distillation of this material (0.01–0.005 mmHg at room temperature), GLPC analysis indicated six different compounds. Preparative GLPC allowed the separation of this mixture into three fractions. From GC/MS analysis, the first two fractions were the dimers and trimers of hexafluoropropene with small amounts of $(CF_3)_2CFH$. Molecular ions (m/e 300 and 450, respectively) and all the expected fragments were observed in the mass spectrum. Mass spectra of the third fraction and the material left in the distillation flask exhibited mass units >450.

The formation of oligomers of hexafluoropropene from the decomposition of $(CF_3)_2CFCdX$ most likely involves the formation of $CF_3CF=CF_2$(HFP) from decomposition of the reagent either via β or α elimination with subsequent fluoride-catalyzed oligomerization of HFP [26].

$$(CF_3)_2CFCdX \xrightarrow{\beta \text{ elimination}} CF_3CF=CF_2 + CdXF$$

$$(CF_3)_2CFCdX \xrightarrow{\alpha \text{ elimination}} [:C(CF_3)_2] \xrightarrow{1,2 \; F\text{-migration [27]}} CF_3CF=CF_2$$

$$+$$

$$CdFX$$

$$CF_3CF=CF_2 + F^- \rightleftharpoons (CF_3)_2CF^- \xrightarrow{CF_3CF=CF_2} \text{HFP (dimers)} + \text{HFP (trimers)}$$

$$(m/e, \; 300) \qquad (m/e, \; 450)$$

When decomposition of the cadmium reagent was carried out in the presence of 2-butene or isobutylene, no 1,1-bis(trifluoromethyl)cyclopropane adduct was detected, indicating β elimination as the most likely decomposition route.

The change of solvent from DMF to acetonitrile caused a remarkable change in the stability of the cadmium reagent. When the cadmium reagent was prepared in CH_3CN, no decomposition was observed even after 15 d at room temperature. However, complete decomposition took place in DMF in 8 h! This stabilization in acetonitrile may be due to the formation of more stable complexes with CH_3CN.

We have observed the formation of two types of perfluoroalkylcopper species on metathesis of copper(I) salts with the corresponding primary F-alkylcadmium reagents [17, 18, 28]. In addition, the formation of $AgCF_3$, $Ag(CF_3)_2^-$ and $Ag(CF_3)_4^-$ on metathesis of silver salts with $(CF_3)_2Cd \cdot glyme$ has also been reported [29]. Detailed investigations, including ^{113}Cd NMR spectroscopy, revealed the two F-alkylcopper reagents to be $R_fCu \cdot CdX_2$ and $(R_f)_2Cu^-$ CdX^+ [28b], respectively. Metathesis of F-isopropylcadmium with copper (I) salts also afforded two copper reagents (a mixture of $(CF_3)_2CFCu$ and $[(CF_3)_2CF]_2Cu^-$) quantitatively.

$$(CF_3)_2CFCdX + CuY \xrightarrow[0\ °C \to RT]{DMF} (CF_3)_2CFCu + [(CF_3)_2CF]_2Cu^-$$
$$(100\%)$$
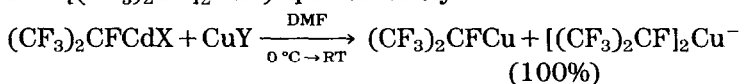
$(X = I/(CF_3)_2CF)$

$(Y = Cl,\ Br,\ I\ or\ CN)$

The distribution of these two perfluoroisopropylcopper reagents depended on which copper(I) salt was employed for the reaction as well as the ratio of the copper(I) salt to the cadmium reagent (see Table 1). For example, when CuCl was employed, $(CF_3)_2CFCu$ was predominantly formed, whereas CuI resulted in $[(CF_3)_2CF]_2Cu^-$ (see Table 1). These two F-alkylcopper species could easily be distinguished in the ^{19}F NMR spectrum. In the case of $(CF_3)_2CFCu$, the ^{19}F NMR resonance for $>CF-Cu$ was at -213.1 (hept) ppm, whereas for $[(CF_3)_2CF]_2Cu^-$ the ^{19}F signal for $>CF-Cu$ appeared at -217.5 (hept) ppm. The ^{19}F NMR chemical shifts of these two copper reagents were similar to the ^{19}F NMR chemical shifts reported for $(CF_3)_2CFAg \cdot CH_3CN$ and $[(CF_3)_2CF]_2Ag^-$ Ag^+ by Burch and Calabrese [7].

Both F-isopropylcopper reagents in DMF were more thermally stable than their cadmium counterparts. At room temperature, under nitrogen, no decomposition was observed after 24 h. On heating, $[(CF_3)_2CF]_2Cu^-$ decomposed faster than $(CF_3)_2CFCu$. For example, after 1.75 h at 80 °C, only 22% of the original $[(CF_3)_2CF]_2Cu^-$ reagent remained in the solution. But in the case of $(CF_3)_2CFCu$, 75% of the original copper reagent remained in solution under the same conditions.

Attempts to functionalize either the F-isopropyl-cadmium or -copper provided little success. In the case of the cadmium reagent, reaction with an alkyl iodide, aryl iodide or even an active substrate like allylbromide did

not yield any of the expected perfluoroalkylated product. Addition of a catalytic amount of copper(I) halide also did not alter the outcome of this reaction. When pyridine was added as the cosolvent, the reaction of $(CF_3)_2CFCdX$ and $PhCOCl$ afforded the corresponding fluorinated ketone [30] in 30% isolated yield.

McLoughlin and Thrower have reported a 40% yield of $PhCF(CF_3)_2$ by heating a mixture of Cu bronze, $(CF_3)_2CFI$ and PhI in DMF at 120 °C [31]. However, in our hands, the pre-formed F-isopropylcopper was found to be unreactive towards the organic substrates despite its thermal stability. No perfluoroalkylated product was observed from the reaction of perfluoroiso-propylcopper with PhI, $BrCH_2CH=CH_2$ or $PhCOCl$ in DMF at room temperature or at 80 °C. In contrast, primary F-alkylcopper reagents, prepared from the metathesis of F-alkylcadmium in DMF, readily afforded fluoroalkylated product with many organic substrates [17, 18]. The lack of reactivity of perfluoro-isopropylcopper is similar to that of the Zn analog reported by Chambers *et al.* [1].

Our attempts to prepare a room-temperature-stable cadmium derivative from the reaction of $CF_3CF_2CFICF_3$ with either Cd or Me_2Cd were not successful. When a mixture of 2-iodononafluorobutane and cadmium powder in DMF was allowed to react at low temperature (-196 °C to room temperature), a rapid exotherm ensued with gaseous evolution; the products were found to be the E/Z isomers of $CF_3CF=CFCF_3$ ($E/Z = \sim 3/1$) by ^{19}F NMR analysis. The reaction of Me_2Cd and $CF_3CF_2CFICF_3$ in CH_3CN (-196 °C to room temperature) also resulted in $CF_3CF=CFCF_3$ ($E/Z = \sim 3/1$) only.

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