Synthesis and properties of donor-free bis(difluoromethyl)cadmium, $(CF_2H)_2Cd$ NMR spectroscopic detection and structure of tetrakis(difluoromethyl)cuprate(III) and related compounds

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Abstract

The reaction of CdR_2 (R = Me, Et) with CF_2HI has been investigated. Insertion of difluorocarbene into Cd–C bonds with formation of 1,1-difluoroethyl, 1,1-difluoropropyl and tetrafluoroethyl derivatives is described. Metathesis of CF_2HI with $CdEt_2$ in non-coordinating solvents gives very reactive, unsolvated $(CF_2H)_2Cd$ in quantitative yield. Spectroscopic and chemical properties are reported. Adducts have been obtained by addition of donors such as diglyme or TMEDA. Partial F vs. Cl exchange with acetyl chloride converts the CF_2H group to CFHCl derivatives. Reaction of $(CF_2H)_2Cd$ with CuCl leads to the formation of thermally unstable (difluoromethyl)copper(I) species, '$Cu(CF_2H)$' and $[Cu(CF_2H)_2]^{\ominus}$. Disproportionation of the cuprate(I) or its oxidation by I_2 or O_2 gives the cuprate(III) anion, $[Cu^{III}(CF_2H)_4]^{\ominus}$, which is stable in water and air. The crystal structure of $[PNP][Cu(CF_2H)_4]$ has been determined. Mixed difluoromethyl/trifluoromethyl cuprates have been prepared from $(CF_3)_2Cu(S_2CNEt_2)$ and $(CF_2H)_2Cd$ in order to verify the square-planar arrangement of substituents by NMR spectroscopy. Identification of compounds was achieved by multinuclear NMR spectra. NMR parameters are discussed.

Keywords: Cadmium; Copper; Fluorine; Difluoromethyl; NMR

1. Introduction

Fluorinated organo derivatives of cadmium and zinc play an important role in the synthesis of fluorinated organic materials [1,2]. In particular, the utility of $(CF_3)_2Cd$ and $(CF_3)_2Zn$ as trifluoromethylation reagents and as difluorocarbene sources has been investigated. The activity of these organometallics in trifluoromethylations is significantly increased by addition of copper(I) halides, and some active CuR_F derivatives have been characterized by NMR spectroscopy. More especially, '$CuCF_3$' has attracted considerable interest not only for its synthetic potential [3], but also because of its facile oxidation to Cu(III) species [4]. A square-planar coordination, as expected for a d^8 complex, has been established for bis(trifluoromethyl)(N,N-diethyldithiocarbamato)copper(III) [4] as well for the tetrakis(tri-

fluoromethyl)cuprate(III) anion [5]. The latter anion has been used recently as the counter ion in tetrathiafulvalene-based organic superconductors, the highest T_c being 9.2 K at ambient pressure [6].

In contrast to the chemistry of perfluorinated organometallics, little is known about partially fluorinated materials. Bis(difluoromethyl)cadmium has been prepared along with $(CF_2H)CdI$ by oxidative addition of CF_2HI to metallic cadmium in DMF [7]. The disadvantage of this preparation route, however, is the low reactivity of the resulting cadmium compound. This may be attributed to complexation of the metal by the strong donor DMF, which cannot be removed without decomposition. Besides its possible potential as a CF_2H transfer reagent, $(CF_2H)_2Cd$, or more generally Cd–CFHX (X = halide) functions are expected to release fluorocarbene, CFH, the chemistry of which has hardly been studied [8,9].

In this contribution we report on the synthesis and some properties of donor-free $(CF_2H)_2Cd$, the detection

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of difluoromethylated Cu(I) and Cu(III) species by means of NMR spectroscopy, as well as on the crystal structure of $[PNP][Cu(CF_2H)_4]$.
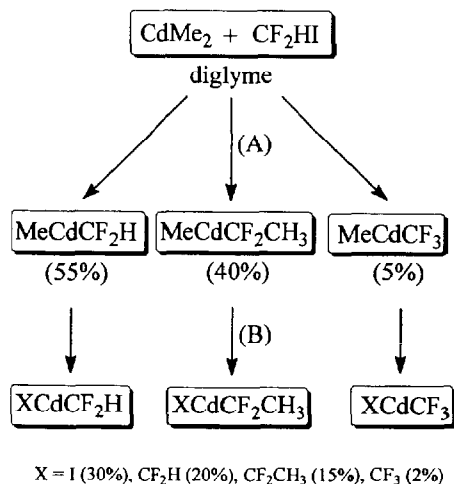
2. Results and discussion

2.1. Difluoromethylcadmium derivatives

Solvated bis(trifluoromethyl)cadmium is readily obtained by the reaction of $CdMe_2$ with CF_3I in presence of a donor solvent such as diglyme, CH_3CN, etc. [10]. Recently, we have reported a facile synthesis of highly reactive donor-free bis(trifluoromethyl)cadmium and its use as low-temperature difluorocarbene source, which made use of the metathesis of CF_3I with $CdEt_2$ [11] following

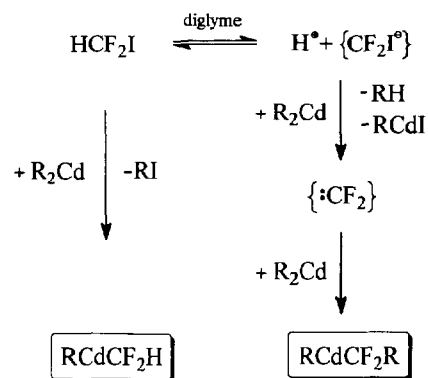$$CdR_2 \xrightarrow[-RI]{+R_FI} R_FCdR \xrightarrow[-RI]{+R_FI} (R_F)_2Cd \qquad (1)$$
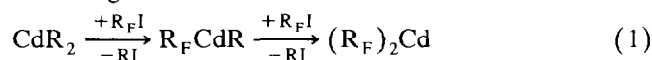
In principle, the same procedure can be applied to CF_2H derivatives, but the exchange proceeds much slower. The low reactivity of CF_2HI was demonstrated by reacting a 1:1 mixture of CF_2HI and CF_3I with $CdMe_2$ — $(CF_3)_2Cd$ being formed exclusively. When $CdMe_2$ is treated with excess CF_2HI in diglyme at ambient temperature, $(CF_2H)CdMe$ is formed within 24 h in a 55% yield along with CH_3CF_2CdMe and CF_3CdMe. The replacement of the second methyl group is much slower and requires ca. 5 days (Scheme 1). Even with very long reaction times no more than 80% of the $Cd–CH_3$ groups are replaced by CF_2R entities, presumably because the intermediately formed MeCdI (Scheme 2) does not react further with CF_2HI.

At ambient temperature the methyl groups bonded to cadmium exchange rapidly. As a consequence the ^1H NMR spectra show only one broad signal for the CH_3 resonance — no Cd satellites being detected. In con-
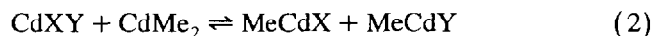

Scheme 2.

trast, the exchange of fluorinated alkyl groups proceeds much slower, e.g. the formation of $(CF_3)(CF_2H)Cd$ from $(CF_3)_2Cd$ and $(CF_2H)_2Cd$ requires several days. If the final product mixture given in Scheme 1 is treated with excess $CdMe_2$, re-formation of the compounds $MeCdCF_2H$, $MeCdCF_2CH_3$ and $MeCdCF_3$ is complete within 1 h

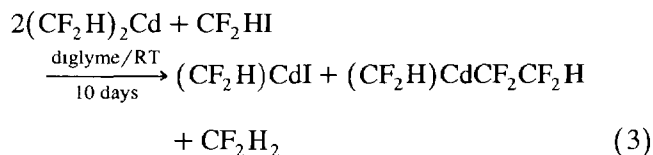$$CdXY + CdMe_2 \rightleftharpoons MeCdX + MeCdY \qquad (2)$$

$(X, Y = I, CF_2H, CF_2CH_3)$

Upon removal of $CdMe_2$ in vacuo the equilibrium (2) is shifted back to the original composition.

As shown in Scheme 1, CF_2CH_3 and CF_3 derivatives are formed in appreciable and minor amounts respectively, by side reactions during CF_2H/CH_3 exchange; thus a complex mixture of CF_2H-, CF_2CH_3- and CF_3-containing species is obtained. The basic distribution $CF_2H : CF_2CH_3 : CF_3$ of 55 : 45 : 5 is preserved during the second step, showing that these groups do not undergo exchange with CF_2HI. The formation of the difluorocarbene insertion product is ascribed to the presence of the polar solvent which favors the dissociation of a proton from CF_2HI (Scheme 2). Indeed, the quantity of methane evolved corresponds to the amounts of CF_2CH_3 derivatives formed. The difluorocarbene formed by iodide transfer to the cadmium inserts selectively into the $Cd–CH_3$ bond. Under these conditions insertion into $Cd–CF_2H$, $Cd–CF_2CH_3$ or $Cd–CF_3$ bonds is not observed.

Difluorocarbene insertion into $Cd–CF_2H$ bonds can be forced, however, by the reaction of excess CF_2HI with $(CF_2H)_2Cd$:

$$2(CF_2H)_2Cd + CF_2HI$$

$$\xrightarrow[10\ days]{diglyme/RT} (CF_2H)CdI + (CF_2H)CdCF_2CF_2H$$

$$+ CF_2H_2 \qquad (3)$$

Scheme 1.

R	XCdCF₂R	XCdCF₂H	total yield	X
Me	40%	55%	75%	I, CF₂H, CF₂CH₃, CF₃
Et	2%	98%	100%	CF₂H

The transformation into the $Cd-CF_2CF_2H$ function proceeds as pointed out in Scheme 2, CF_2H_2 now being the volatile product. After 10 days the $(CF_2H)_2Cd$ is converted almost quantitatively to an equilibrium mixture containing $(HCF_2CF_2)_2Cd$ and $(HCF_2CF_2)CdI$ along with some CdI_2. Only traces of trifluoromethylation products such as $CF_3CdCF_2CF_2H$ are observed.

Replacement of $CdMe_2$ by the more reactive $CdEt_2$, Eq. (1), gives $(CF_2H)_2Cd$ in almost quantitative yield. The difluorocarbene insertion pathway which leads to $(CF_2H)CdCF_2CH_2CH_3$ now accounts for only 2% of the reaction products. If polar conditions are avoided, the formation of CF_2 insertion products is suppressed completely. Thus, if CH_2Cl_2 or excess CF_2HI is used as solvent, pure donor-free $(CF_2H)_2Cd$ precipitates as a white powder, which is slightly soluble in CH_2Cl_2, $CHCl_3$ or toluene and explodes violently upon contact with air.

$$CdEt_2 + 2CF_2HI \xrightarrow[5 \ min]{CH_2Cl_2/RT} (CF_2)_2Cd + 2EtI \qquad (4)$$
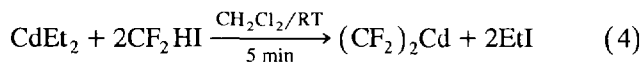
While donor-free $(CF_3)_2Cd$ decomposes above -5 °C to CdF_2 and CF_2, bis(difluoromethyl)cadmium is stable below 90 °C. Heating to 98 °C results in a slow evolution of gases which, according to NMR analyses, mainly consist of ethylenes ($F_2C=CH_2$ 25%, $FHC=CH_2$ 21%, $F_2C=CFH$ 15%, C_2F_4 9%, cis-HFC=CFH 9%, trans-HFC=CFH 5%, C_2H_4 5%, CF_2H_2 10%, and CH_3F less than 1%). At 100 °C the material explodes with emission of light and formation of carbon, metallic cadmium and gases mainly consisting of 1,1,2,2-tetrafluoroethane.

The Raman spectrum of $(CF_2H)_2Cd$ shows the characteristics of the CF_2H group [12,13] with ν(CH) at 2965 cm^{-1}, ρ(CH) 1316 (b_g)/1301 (a_g) cm^{-1}, ν_s(CF$_2$) 1007 cm^{-1}, ν_{as}(CF$_2$) 864 cm^{-1}, δ(CF$_2$) 536 cm^{-1}, ν_s(CdC) and ω(CF$_2$) at 483 and 190 cm^{-1}, the latter two being coupled strongly. The infrared spectrum of a nujol or Kel-F mull shows corresponding absorptions at 2964, 1291, 1006, 866 and 530 cm^{-1}. As for $(CF_3)_2Cd$, the low CF stretch frequencies point toward significant association via $C-F \cdots Cd$ contacts, in accord with the observation that the compound does not sublime.

Addition of stoichiometric amounts of a donor yields the corresponding adduct

$$(CF_2H)_2Cd + D \rightarrow (CF_2H)_2Cd \cdot D \qquad (5)$$
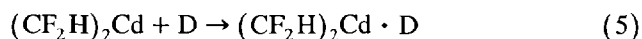
(D = diglyme, $2CH_3CN$, 2DMF, 2PMe$_3$, TMEDA, TMPDA)

The adducts with diglyme, PMe$_3$ and DMF are liquids which freeze to glassy solids between 10 to 15 °C and which may be handled for short times in air. Upon heating in vacuo to 70 °C CF_2H_2 is eliminated. With CH_3CN or dioxane, solids are formed which explode upon contact with the air and from which the ligand can be stripped off in vacuo without decomposition of the

$(CF_2H)_2Cd$ moiety. The solid adducts with tetramethylethylenediamine (TMEDA) or tetramethylpropylenediamine (TMPDA) slowly degrade in air with loss of the ligand and final formation of CdF_2; upon heating they decompose exothermically at 70 and 140 °C respectively. Solutions of $(CF_2H)_2Cd$ in diglyme react exothermically with O_2 to formyl fluoride and CdF_2, similar to the oxidation of $(CF_3)_2CFAg$ to $(CF_3)_2C=O$ [14].

It has been reported that the elimination of difluorocarbene from $(CF_3)_2Cd$ in diglyme may be forced at -30 °C by treatment with acetyl bromide, AcBr [15], $CdCF_2Br$ groups presumably being formed intermittently. However, if $(CF_2H)_2Cd$ is treated with AcCl in diglyme at ambient temperature, hitherto unknown (chlorofluoromethyl)cadmium compounds are obtained.

$$(CF_2H)_2Cd \xrightarrow[-AcF]{AcCl/diglyme/RT} (CFHCl)CdX \qquad (6)$$
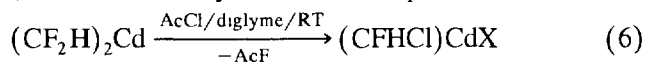
(X = Cl, CFHCl)

After 8 h at ambient temperature the conversion is complete with a total yield of up to 80% of $(CFHCl)_2Cd$ (meso- and rac-isomers, ca. 1:1) and (CFHCl)CdCl in a 1:1 ratio. By-products are AcCF$_2$H, AcCFHCl as well as cis- and trans-1,2-difluoroethylene (3:1). Reaction of $(CF_2H)_2Cd$ with Me$_3$SiCl proceeds similarly but results in considerably lower yields of (CFHCl)$_2$Cd and (CFHCl)CdCl. An NMR study of reaction (6) suggests that CFH inserts into Cd–Cl bonds, in analogy to the formation of $Cd(CH_2Cl)_2$ from diazomethane and $CdCl_2$ [16]. Thus, $(CF_2H)CdCl$ and cis/trans-difluoroethylene are the major products formed initially. Once appreciable amounts of the Cd–Cl function are generated, the formation of the ethylenes levels off as CFH insertion
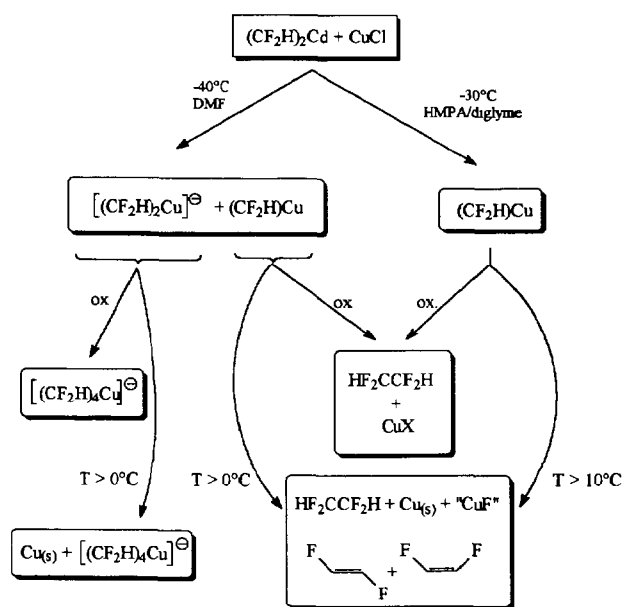

Scheme 3.

into the Cd–Cl bond becomes competitive. After $(CF_2H)_2Cd$ has disappeared completely, the intermittently formed $(CF_2H)Cd(CFHCl)$ is converted to $(CFHCl)CdCl$ and finally $(CFHCl)_2Cd$. Attempts to trap CFH with electron-rich double bond systems have been unsuccessful. Furthermore, if AcBr was reacted with $(CF_2H)_2Cd$ in the presence of $CdCl_2$, no evidence for Cd–CFHCl functions was found; instead, new ^{19}F NMR patterns ascribed to Cd–CFHBr derivatives were detected along with AcF, $AcCF_2H$, AcCFHBr and cis/trans-1,2-difluoroethylene. It is therefore concluded that the mechanism does not involve free CFH.

2.2. Difluoromethylcopper derivatives

Allyl bromide is quantitatively converted to 4,4-difluoro-1-butene by treatment with $(CF_2H)_2Cd$ in diglyme at ambient temperature for 3–5 h. However, if the reaction is carried out in the presence of stoichiometric amounts of copper(I) chloride, it is finished within 30 min at a temperature of $-30\ °C$.

$$\diagdown\!\!=\!\!\diagup\!\!-Br \xrightarrow[-30°C/30\ min/diglyme]{(CF_2H)_2Cd/CuCl} \diagdown\!\!=\!\!\diagup\!\!-CF_2H \qquad (7)$$
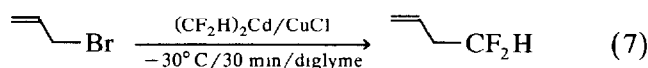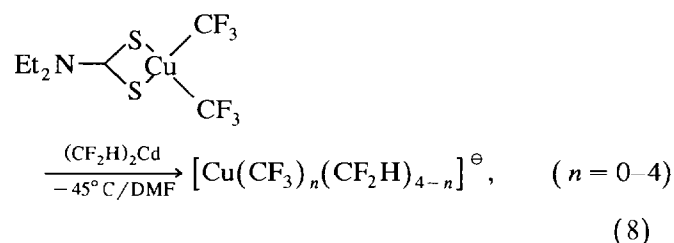
The increased reaction rate is associated with the formation of very reactive (difluoromethyl)copper species which are readily detected by ^{19}F NMR spectroscopy at low temperatures. Their formation and characteristics strongly parallel those of trifluoromethyl [17] or other perfluoroalkyl copper species [18]. Thus, a species containing one CF_2H group, presumably complexed by chloride and/or solvent and denoted $Cu(CF_2H)$ in the following, as well as the cuprate(I) $[Cu(CF_2H)_2]^{\ominus}$ are formed from $(CF_2H)_2Cd$ and CuCl in DMF at $-40\ °C$ or in a mixture of DMSO and diglyme at $-25\ °C$ (Scheme 3). If HMPA is added, we note a small but distinct increase in both the thermal and chemical stability of $Cu(CF_2H)$, and only traces of $[Cu(CF_2H)_2]^{\ominus}$ are detected. The thermal decomposition of $Cu(CF_2H)$ in HMPA–diglyme proceeds via two competing pathways: (1) reductive coupling to HF_2CCF_2H and metallic copper, and (2) fluoride abstraction and evolution of cis- and trans-difluoroethylene. Insertion of fluorocarbene into a Cu–C bond as found for $CuCF_3$ [19] does not occur. Oxidation of $Cu(CF_2H)$ with oxygen, iodine or tetraethylthiuram disulfide, $[Et_2NC(S)S]_2$, gives HF_2CCF_2H.

Warming of the bis(difluoromethyl)cuprate(I) anion in DMF or DMSO–diglyme above 0 °C results in disproportionation to metallic copper and tetrakis(difluoromethyl)cuprate(III). The same anion is also obtained by oxidation of the cuprate(I) with O_2 or preferentially I_2 (Scheme 3). Use of excess I_2 or Br_2 leads to decomposition and formation of CF_2HX. Whereas these reactions are fully consistent with the behavior of the

corresponding CF_3 cuprate [5], the oxidation with tetraethylthiuram disulfide does not yield the $(N,N$-diethyldithiocarbamato)copper(III) complex but solely $[Cu(CF_2H)_4]^{\ominus}$. The same result, formation of $[Cu(CF_2H)_4]^{\ominus}$, is obtained if $(Et_2NCS_2)Cu^{III}Br_2$ is reacted with $(CF_2H)_2Cd$, even with a large excess of the copper compound. The different reactivities of $(CF_3)_2Cd$ and $(CF_2H)_2Cd$ toward $(Et_2NCS_2)Cu^{III}Br_2$ are apparent from the reaction conditions. Whereas $(CF_3)_2Cd$ requires ca. 5 min at ambient temperature, a frozen DMF solution of bis(difluoromethyl)cadmium reacts immediately upon melting $(-60\ °C)$. A similar increase in reactivity is observed for the generation of the Cu(I) moieties; that is, the quantitative formation of the $CF_3Cu(I)$ species requires prolonged reaction times at $-30\ °C$ or several minutes at 20 °C, whereas the exchange between $(CF_2H)_2Cd$ and CuCl is complete immediately after mixing at $-40\ °C$.

The tetrakis(difluoromethyl)cuprate(III) was isolated as its PNP salt in the form of colorless crystals with a total yield of 20%. The yield of the oxidation is enhanced to 80% by addition of TMEDA which, however, could not be separated quantitatively from the product. Like its CF_3 analog, it is not sensitive to air and moisture. At 152 °C $[PNP][Cu(CF_2H)_4]$ decomposes exothermically with loss of 17.8% of its weight corresponding to the formation of $[PNP][CuF_3]$ (Δm_{calc} 18.2%), in accord with the degradation of $Bu_4N[Cu(CF_3)_4]$ to $Bu_4N[CuF_3]$ [5].

In order to prove the identity of the tetrakis(difluoromethyl)cuprate(III) by means of NMR spectroscopy (see below) we have prepared mixed CF_3/CF_2H cuprates. The high reactivity of $(CF_2H)_2Cd$ enables the elimination of the N,N-diethyldithiocarbamate ligand from $(CF_3)_2Cu(S_2CNEt_2)$ at $-45\ °C$. The resulting product mixture contains all possible $[(CF_3)_nCu(CF_2H)_{4-n}]^{\ominus}$ species, which are converted to their PNP salts by treatment with [PNP]Cl.

$$Et_2N\!-\!\!\!\diagup\!\!\!\!\!\begin{smallmatrix}S\\ \\ S\end{smallmatrix}\!\!\!\!\diagup\!Cu\!\diagup\!\!\!\!\begin{smallmatrix}CF_3\\ \\ CF_3\end{smallmatrix}$$

$$\xrightarrow[-45°C/DMF]{(CF_2H)_2Cd} \left[Cu(CF_3)_n(CF_2H)_{4-n}\right]^{\ominus}, \qquad (n = 0\text{–}4)$$
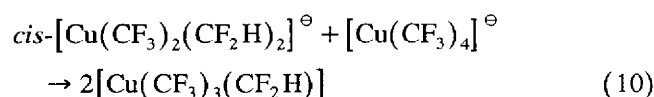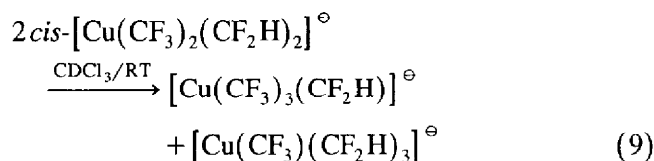
$$(8)$$

The planar skeleton of the d^8 complexes is evident from the NMR spectroscopic detection of the species with $n = 1$ and $n = 3$ showing the presence of two chemically different CF_2H and CF_3 groups respectively. Following the NMR analysis (see below), the major component is trans-$[Cu(CF_3)_2(CF_2H)_2]^{\ominus}$ (58%). Whereas the signals of $[Cu(CF_2H)_4]^{\ominus}$ (2%) and $[Cu(CF_3)(CF_2H)_3]^{\ominus}$ (12%) slowly decline at room temperature, the amount of trans-$[Cu(CF_3)_2(CF_2H)_2]^{\ominus}$ re-

Table 1
NMR data of difluoromethylcadmium derivatives, $(CF_2H)CdR$ [a]

R	$\delta(^{113}Cd)$	$\delta(^{19}F)$	$\delta(^1H)$	$\delta(^{13}C)$	$^2J(FH)$	$^2J(^{113/111}CdF)$	$^2J(^{113/111}CdH)$	$^1J(CF)$	$^1J(^{113/111}CdC)$	$^3J(CF)$	$^1J(CH)$
CH_2CH_3 [c]	−332.4	−120.4	6.1	149.0	43.2	265/254	68.7/65.7	283.3	990/946	–	154.7
CH_3	−270.5	−120.2	6.2	150.3	43.0	275/263	70.3/67.2	281.0	1074/1026	–	155.6
CF_2CH_3	−454.5	−119.7	6.2	147.9	43.0	293/281	84.9/81.2	283.0	–[b]	5.5	–[b]
CF_2H [d]	−463.1	−119.9	6.2	146.1	43.4	294/281	85.4/81.7	282.5	1257/1203	5.7	157.7
CFHCl [e]	−460.8	−119.4	6.3	145.6	43.2	304/290	95.5/91.3	283.2	–[b]	4.4	–[b]
CF_3 [f]	−478.8	−119.6	6.3	144.3	43.5	318/304	102.1/97.6	281.9	1679/1605	5.9	159.4
X [g]	−469.4	−118.6	6.4	144.6	43.0	361/345	135.0/129.1	286.0	1773/1695	–	161.1

[a] In diglyme with C_6D_6 as internal lock. Chemical shifts are in ppm, coupling constants in Hz. References are external TMS, $CFCl_3$ and $CdMe_2$. [b] Not observed. [c] $\delta(C^1H_2)$ 0.25 ppm, $\delta(C^1H_3)$ 1.2 ppm, $\delta(^{13}CH_2)$ 3.1 ppm, $\delta(^{13}CH_3)$ 13.4 ppm, $^3J(HH)$ 8.1 Hz, $^2J(CdH)$ 69.0/65.9 Hz, $^3J(CdH)$ 68.9/65.8 Hz, $^1J(CH_2)$ 123.7 Hz, $^1J(CF)$ 3.8 Hz, $^3J(CH_3)$ 123.3 Hz, $^1J(CdC)$ 785/751 Hz, $^2J(CdC)$ 29.5 Hz. [d] $^3J(CH)$ 2.1 Hz; Simulation as $[AX_2]_2$ spin system yields: $^2J(AX) + 43.4$ Hz, $^4J(XX')$ ± 1.2 Hz, $^4J(AX')$ $+0.2$ Hz, $^4J(AA')$ 0.0 Hz; ^{19}F NMR data in CD_2Cl_2: $\delta(^{19}F)$ −120.0 ppm, $^2J(^{113}CdF)$ ca. 310 Hz, $^2J(HF)$ 43.1 Hz, $\delta(^1H)$ 6.4 ppm, $^2J(CdH)$ ca. 100 Hz. [e] $\delta(C^{19}F_3)$ −35.6 ppm, $^2J(^{113/111}CdF)$ 422/403 Hz. [g] X = Cl, Br or I; data are independent of the nature of the halide. [f] $\delta(C^{19}F)$ −120.0 ppm, $^2J(^{113}CdF)$ ... $J(AX) + 43.4$ Hz, $^4J(XX')$ ... $^2J(AX)$ 69.0/65.9 Hz, $^3J(CdH)$ ... Simulation as $[AX_2]_2$ spin system yields: $^2J(AX)$ ... $^4J(FF)$ 0.7 Hz.

mains unchanged for several days. The cis isomer (23%) seems to be involved in a slow scrambling reaction both with itself, Eq. (9), and with $[Cu(CF_3)_4]^\ominus$ (2%), eq. (10); theses reactions result in complete loss of the cis isomer and the otherwise stable $[Cu(CF_3)_4]^\ominus$ and in a considerable increase of the initial $[Cu(CF_3)_3(CF_2H)]^\ominus$ (3%) concentration.

$$2\,cis\text{-}\left[Cu(CF_3)_2(CF_2H)_2\right]^\ominus$$

$$\xrightarrow{\text{CDCl}_3/\text{RT}} \left[Cu(CF_3)_3(CF_2H)\right]^\ominus$$

$$+\left[Cu(CF_3)(CF_2H)_3\right]^\ominus \qquad (9)$$

$$cis\text{-}\left[Cu(CF_3)_2(CF_2H)_2\right]^\ominus + \left[Cu(CF_3)_4\right]^\ominus$$

$$\rightarrow 2\left[Cu(CF_3)_3(CF_2H)\right] \qquad (10)$$

2.3. NMR spectra

The variety and abundance of NMR-active nuclei (^{1}H, ^{19}F, ^{13}C and ^{113}Cd/^{111}Cd) facilitates the unambiguous identification of even minor compounds in complex mixtures. The NMR parameters of difluoromethyl, 1,1-difluoroalkyl, chlorofluoromethyl, and tetrafluoroethyl cadmium derivatives are set out in Tables 1–4. ^{19}F NMR spectroscopy is especially of high analytical value owing to its sensitivity, the wide range of chemical shifts and its resolvable long range couplings with characteristic multiplicities. The difluoromethyl groups are easily recognized by their doublet (^{19}F) and triplet structures (^{1}H) with ^2J(FH) being rather constant at 43 Hz. Couplings across the metal atom are not or barely resolvable for ^4J(HH) (less than 0.5 Hz) and ^4J(FH) respectively, whereas the ^4J(FF) couplings yield valuable information about the second fluoroalkyl group attached to cadmium. For $(CF_2H)_2Cd$ a characteristic high-order pattern of the $[A[X]_2]_2$ spin system is observed, similar to that in bis-difluoromethyl derivatives of silicon [13] or tin [20].

The couplings of fluorine to cadmium (^2J(CdF)) as well as the less readily accessible ^1J(CdC), apparent from the characteristic double pair of cadmium satellites (^{113}Cd 12.3%, ^{111}Cd 12.8%; $\gamma(^{113}$Cd)/$\gamma(^{111}$Cd) = 1.046), are extremely sensitive to substituent effects and

mainly reflect the demand for metal 5s character [21]. In general, the largest couplings are found for the halides. Line broadening and the insensitivity of the data to the nature of the halide hint at fast exchange of the halide and ionic bonding, $R_FCd^+X^-$, respectively. Competition for Cd(5s) character increases with increasing covalence of the second Cd–C bond, the lowest value for ^2J(CdF) being found for the ethyl derivative. A comparison of the ^2J(CdF) coupling constants in CF_3 and CF_2H compounds, displayed in Fig. 1, shows that these trends are well correlated, $^2J(CdCF_3) \propto 1.7\,^2J\text{-}(CdCF_2H)$. Similar dependencies are found for the other partly fluorinated moieties.

Relative signs of the coupling constants have been determined by selective decoupling experiments and by two-dimensional (2D) techniques. Fig. 2 shows a ^{19}F/^{13}C–2D spectrum, proving that ^2J(HF) is positive (with respect to the positive ^1J(CH) coupling) and that ^1J(CdC) and ^2J(CdF) have the same (negative) sign. Furthermore, the corresponding ^{1}H/^{13}C–2D correlation yields a negative sign for the ^2J(CdH) coupling. This result is in contrast to the positive sign found for $CdCH_3$ derivatives, γ(Cd) < 0, but it is in accord with results obtained for CF_2H derivatives of other NMR-active metals [22].

The ^{19}F NMR spectrum of the CFHCl group of $(CFHCl)_2Cd$ and $(CF_2H)Cd(CFHCl)$ displayed in Fig. 3 shows that these groups are readily recognized in high-resolution spectra by their characteristic chlorine isotope pattern with a shift difference, $^{35}Cl-^{37}Cl$, of 0.012 ppm. Furthermore, two resonances are found for the first compound and assigned to the meso- and rac-diastereomers; however, no such distinction was possible in the ^{13}C or ^{113}Cd spectra.

The ^{113}Cd shifts of the fluoroalkyl cadmium compounds are found in a rather narrow range of − 440 to − 480 ppm and are clearly set off from the alkyl substituted derivatives which resonate at higher frequencies (Table 1). These trends are in accord with those reported on other fluoroalkyl cadmium compounds [23]. The ^{13}C resonances of the CF_2H, and more generally the CF_2R groups, fall in the same region as that of the CF_3 group, ca. 150 ppm.

The ^{19}F resonances of the copper derivatives (Table

Table 2
NMR data of (chlorofluoromethyl)cadmium derivatives, (CFHCl)CdR [a]

R	$\delta(^{113}\text{Cd})$	$\delta(^{19}\text{F})$	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	^2J(FH)	$^2J(^{113/111}\text{CdF})$	$^2J(^{113/111}\text{CdH})$	^1J(CF)	^3J(CF)
CF_2H [c]	− 460.8	− 155.7	6.11	118.9 [d]	43.4	227/217	42.2/40.3	281.7	5.7
CFHCl [e]	− 457.4	− 155.3	6.13	118.4	43.4	236/225	46.3/44.3	282.1	4.4
X [f]	− [b]	− 153.8	6.14	117.0	43.3	299/286	− [b]	284.3	−

[a] See Table 1; isotope shift $\Delta\delta(CF^{35}Cl-CF^{37}Cl)$ 0.012 ppm. [b] Not observed. [c] ^4J(FF) 0.7 Hz. [d] ^1J(CdC) 1251/1196 Hz. [e] |$\Delta\delta$(meso − rac)| 0.0092 ppm. [f] X = Cl, Br or I; the data does not depend on the halide.

Table 3
NMR data of (1,1-difluoroalkyl)cadmium derivatives, $RCdCF_2CH_3$ and $RCdCF_2CH_2CH_3$ [a]

R	$\delta(^{113}Cd)$	$\delta(^{19}F)$	$\delta(C^1H_3)$	$\delta(^{13}CF_2)$	$\delta(^{13}CH_3)$	$^3J(FH)$	$^2J(^{113/111}CdF)$	$^3J(CdH)$	$^1J(CF)$	$^3J(CF)$	$^2J(CF)$	$^2J(^{113/111}CdC)$
$RCdCF_2CH_3$ [c]												
CH_3 [d]	−280.8	−77.6	1.5	153.7	31.3	28.7	323/309	23.2	286.8	−	17.4	56.0/53.5
CF_2CH_3	−455.0	−76.6	1.5	151.3	30.8	28.7	345/330	26	287.0	5.5	17.4	62.7/59.9
CF_2H	−454.5	−77.0	1.5	151.0	30.7	28.5	347/332	26	287.0	5.5	17.4	62.8/60.0
CF_3 [e]	−[b]	−76.3	−[b]	−[b]	−[b]	28.6	372/356	−[b]	−[b]	−[b]	−[b]	−[b]
X	−[b]	−75.8	1.5	151.5	30.7	28.5	426/407	32.0	289.0	−	17.0	70.3/67.1
$RCdCF_2CH_2CH_3$ [f]												
CH_2CH_3	−[b]	−85.9	−[b]	−[b]	−[b]	23.8	286/273	−[b]	−[b]	−[b]	−[b]	−[b]
$CF_2CH_2CH_3$ [g]	−439.9	−85.3	0.9	156.8	10.9	23.9	311/298	−[b]	292.9	6.6	16.7	65.4/62.5
CF_3 [h]	−[b]	−84.3	1.1	−[b]	−[b]	23.9	345/330	−[b]	−[b]	−[b]	−[b]	−[b]
X [i]	−460.3	−82.0	0.9	155.4	11.0	23.9	428/409	−[b]	295.9	−	16.1	77.6/74.2

[a] See Table 1. [b] Not observed. [c] Invariant data: $^3J(CF)$ 5.5 Hz. [d] $^1J(^{113/111}CdCdCF_2Me)$ 1101/1050 Hz, $^3J(H_3CCdCF_2Me)$ 2.1 Hz. [e] $\delta(C^{19}F_3)$ −35.4 ppm, $^2J(^{113/111}CdF)$ 415/397 Hz.
[f] Invariant data: $\delta(C^1H_2)$ 1.7–1.8 ppm, $\delta(^{13}CH_2)$ 39 ppm, $^3J(HH)$ 7.3–7.6 Hz, $^2J(CF_2CH_2)$ 4 Hz, $^2J(CF_2CH_2CH_3)$ 7 Hz, $^3J(CF_2CH_2CH_3)$ 9 Hz, $^3J(CdC)$ 9 Hz. [g] $^1J(^{113/111}CdC)$ 1777/1691 Hz.
[h] $\delta(C^{19}F_3)$ −34.7 ppm, $^2J(^{113/111}CdF)$ 411/393 Hz. [i] $^1J(^{113/111}CdF)$ 1281/1225 Hz, $^3J(FCCdCF_2Et)$ 6.6 Hz.
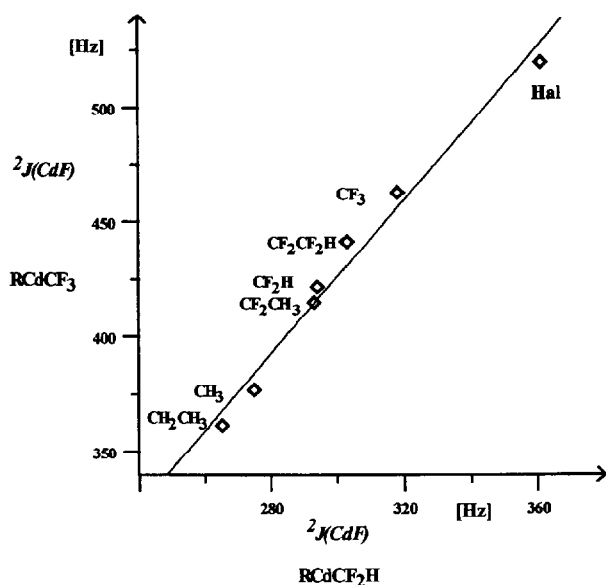
Fig. 1. Correlation of ^2J(CdF) coupling constants in CF_3CdR and CF_2HCdR derivatives.

decoupled ^{13}C spectra which show a triplet (^1J(CF)) for $Cu(CF_2H)$ and a triplet of triplets (^1J(CF)/^3J(CF)) for $[Cu(CF_2H)_2]^{\ominus}$.

Inspection of the data in Table 5 reveals pronounced differences between Cu(I) and Cu(III) species. The coupling constants ^1J(CF), ^1J(CH) and ^2J(FH) are significantly larger for the Cu(III) compounds. This tendency is opposite to that found for CF_3 derivatives of main Group IV elements where ^1J(CF) is significantly larger in divalent Ge, Sn or Pb derivatives than in their tetravalent compounds [24]. Similarly, the ^{13}C resonance is shifted to low frequencies, again opposite to the trend in main group chemistry.

Since the $[A[X]_2]_4$ spin system of the $[Cu(CF_2H)_4]^{\ominus}$ anion is too complex for a detailed analysis, and since the broad ^{13}C signal did not yield any structural information, mixed CF_3/CF_2H species have been used to prove the square-planar arrangement of the copper atom (Table 6). The variation in ^{19}F chemical shifts is surprisingly high, spanning a range of 7 ppm for the CF_3 and 15 ppm for the CF_2H resonances. Both CF_3 and CF_2H resonances are shifted to low frequencies as the number of CF_2H groups increases. Assignments and connectivities of the complex multiplets were verified by selective decoupling experiments. The most valuable information based on resolvable ^4J(FF) couplings is gained from the asymmetric cuprates containing three CF_3 or three CF_2H groups. For example, three resonances at -36.3, -38.8 and -100.4 ppm with relative intensities of $3:6:2$ could be assigned to the $[Cu(CF_3)_3(CF_2H)]^{\ominus}$ anion. The trans-CF_3/CF_2H coupling was obtained by decoupling of the signal at -38.8 ppm. Decoupling of the fluorines of the CF_3 group trans to the CF_2H group results in a $[A_3X]_2M$
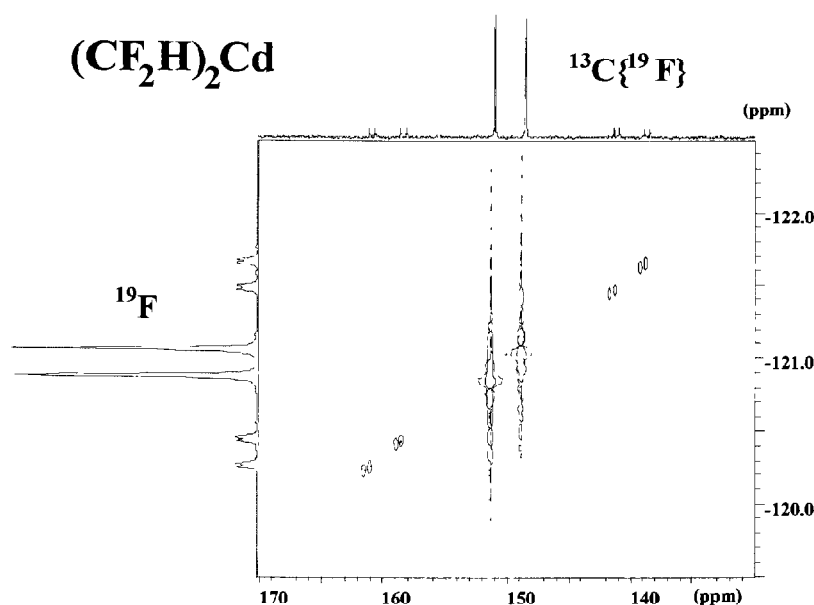
5) exhibit temperature-independent broadening (line widths of 3–5 Hz) which hides details of high-order spectra. Both $Cu(CF_2H)$ and $[Cu(CF_2H)_2]^{\ominus}$ give rather broad ($\Delta\nu$ ca. 4 Hz) doublets due to ^2J(FH) coupling — no indication of a $[A[X]_2]_2$ spin system being detected for the latter anion. In accord with the value of 1.2 Hz found for isoelectronic $(CF_2H)_2$Cd, a small value of ^4J(FF) (less than 2 Hz) was confirmed by inspection of the ^{13}C satellites which are hardly broadened additionally. The number of CF_2H groups attached to copper is, however, clearly evident from the ^1H

Fig. 2. 2D-$^{13}C/^{19}F$–COSY spectrum of $(CF_2H)_2$Cd. The signs of ^2J(CdF) and ^1J(CdC) as well those of ^1J(CH) and ^2J(FH) are equal.

Table 4

NMR data of (tetrafluoroethyl)cadmium derivatives, $(HCF_2CF_2)CdR$ [a]

R	$\delta(^{113}Cd)$	$\delta(CF_2)$	$\delta(CF_2H)$	$\delta(CF_2)$	$\delta(CF_2H)$	$^2J(^{113/111}CdF)$	$^3J(CdF)$	$^3J(CdH)$	$^1J(^{113/111}CdC)$	$^2J(^{113/111}CdC)$
CF_2H [c]	−454.0	−115.8	−129.5	142.9	114.3	242/232	24	33	1115/1066	36.0/34.4
CF_2CF_2H [d]	−442.4	−115.2	−129.6	142.9	114.4	256/245	29	39	1220/1166	37.7/36.0
CF_3	− [b]	−114.8	−129.7	− [b]	− [b]	261/250	30	− [b]	− [b]	− [b]
X	−443.5	−113.4	−130.1	142.5	114.1	323/309	34	51	1559/1490	40.2/38.6

[a] See Table 1; invariant NMR data: $\delta(CF_2H)$ 5.4 ppm, $^1J(CF_2H)$ 188 Hz, $^2J(FH)$ 59 Hz, $^2J(CF_2CF_2H)$ 32 Hz, $^3J(FH)$ 7.6 Hz, $^3J(FF)$ 3.6 Hz, $^2J(CH)$ 1.7 Hz. [b] Not observed. [c] $^3J(CH)$ 2.1 Hz. [d] $^4J(CH)$ 0.8 Hz.

spin system $(M = {}^1H)$ from which an averaged cis-CF_3/CF_2H coupling was extracted. Finally, the cis-$^4J(FF)$ coupling between the CF_3 groups was obtained by irradiation of the CF_2 group. For the anion $[CuCF_3(CF_2H)_3]^\ominus$ a doublet $(^2J(FH))$ of quartets $(^4J(FF))$ is found for the group trans to CF_3, since the coupling between the non-equivalent CF_2H groups is smaller than the linewidth of ca. 2 Hz. Decoupling of the CF_3 resonance gives a doublet for the trans-CF_2H group and an $[A[X]_2]_2$ spin system for the cis-CF_2H groups.

In general, the main features of the signals are determined by trans couplings. This observation was used to assign the ^{19}F signals of the trans and cis isomers of bis(difluoromethyl)bis(trifluoromethyl)cuprates(III). In the proton decoupled ^{19}F spectra the resonances of the CF_3 and CF_2H groups respectively appear as quintets and septets for both anions. The assignment of the trans

configurated cuprate is based on the large coupling between the two CF_2H groups with an averaged value of 10 Hz for $^4J(FF)$ and $^4J(FF')$, gained from the analysis of the $[A[X]_2]_2$ spin system of the CF_3 decoupled spectrum. In contrast, the line shape analysis of the corresponding signal of the other isomer gave a value of only ca. 2 Hz, which suggests a cis arrangement of the CF_2H groups. The pseudo-quintet and septet structures in the ^1H decoupled spectrum of the cis isomer are in accord with an analysis as an $[A_3X_2]_2$ spin system where $J(AX) + J(AX') = 11.7$ Hz and $J(AX) \sim 2\ J(AX')$.

2.4. Description of the crystal structure

Crystals of $[PNP][Cu(CF_2H)_4]$ consist of widely separated ions. The structure of the cation with its bent

Table 5

NMR data of difluoromethylcopper compounds

	$\delta(^{19}F)$	$\delta(^1H)$	$\delta(^{13}C)$	$^2J(FH)$	$^1J(CF)$	$^1J(CH)$	$^3J(CF)$
$Cu(CF_2H)$ [a]	−112.8	6.1	148.5	44.7	265	148	−
$[Cu(CF_2H)_2]^-$ [a]	−116.6	6.0	151.1	44.4	257	143	4.2
$[Cu(CF_2H)_4]^-$ [b]	−115.8 −114.9 [a]	6.2	138.3	48.6	296	165	− [c]

[a] In DMSO–diglyme, internal lock: C_6D_6, spectra recorded at 263 K. [b] As $PNP[Cu(CF_2H)_4]$ in $CDCl_3$ at 298 K, $[A[X]_2]_4$ spin system, see also Table 6 and text. [c] Not resolved.

Table 6

^{19}F NMR data of mixed (difluoromethyl)(trifluoromethyl)cuprates(III), $[(CF_3)_nCu(CF_2H)_{4-n}]^\ominus$ [a]

	$\delta(C^{19}F_3)$ [b]	$\delta(C^{19}F_2H)$ [b]	$^2J(HF)$	$^4J(FF)$			
				cis-CF_3/CF_2H	trans-CF_3/CF_2H	cis-CF_2H/CF_2H	trans-CF_2H/CF_2H
$[Cu(CF_2H)_4]$	−	115.6 [c]	50.0 [d]	−	−	< 2	ca. 6 [c]
$[(CF_3)Cu(CF_2H)_3]^-$	−41.9	−110.3 [c] −113.3	50.2 [d] 48.3	2.3	6.9	< 2	7.6
trans-$[(CF_3)_2Cu(CF_2H)_2]^-$ [f]	−40.9	−107.8	49.6 [d]	4.2	−	−	8/12 [g]
cis-$[(CF_3)_2Cu(CF_2H)_2]^-$	−39.8	−107.1	48.3 [d]	3.9	7.8	ca. 2	−
$[(CF_3)_3Cu(CF_2H)]^-$	−36.3 [h] −38.8	−100.4	48.4	5.3	10.9	−	−
$[(CF_3)_4Cu]^-$	−35.1	−	−	−	−	−	−

[a] As PNP salts in $CDCl_3$ at RT. [b] For multiplicities and analyses see text. [c] Appearance similar to a $[AX_2]_2$ system with a trans-$^4J(FF)$ coupling of ca. 6 Hz and non-resolved cis-coupling. [d] Value for $^2J(FH) + ^4J(FH)$ with $^4J(FH) \sim 1.5$ Hz for trans-CF_2H groups. [e] CF_2H group trans to CF_3. [f] ^{13}C data are: $\delta(CF_3)$ 140.4 ppm, $\delta(CF_2H)$ 135.1 ppm, $^1J(CH)$ 175 Hz. [g] From CF_3 decoupled spectrum, simulated as $[A[X]_2]_2$ spin system. [h] CF_3 group trans to CF_2H, $^4J(cis-CF_3/CF_3)$ 5.7 Hz.
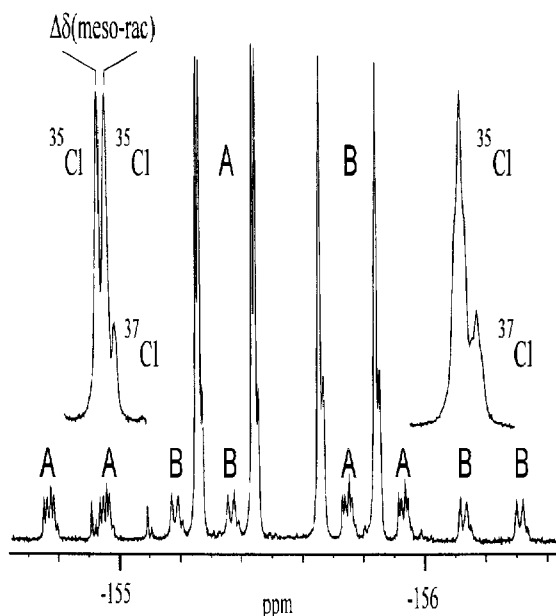
Fig. 3. ^{19}F NMR spectrum of the CFHCl fragments of (CFHCl)$_2$Cd (A) and (CFHCl)CdCF$_2$H (B) with $^{113/111}$Cd satellites. Expansions show signals for the meso- and rac-isomers of (A) as well as chlorine isotope patterns.

P–N–P backbone (137.4(3)°) and P–N bond lengths averaging 1.581(4) Å is not unusual. The anion possesses a CuC$_4$ core which is planar to within ±0.04 Å, and this coordination plane roughly bisects the F–C–F angles of the CHF$_2$ groups — the fluorine atoms lying between 0.59(1) and 1.23(1) Å from the plane. The Cu–C bond lengths (Table 7) average 1.932(15) Å, a value slightly, but not significantly, shorter than that in [PNP][Cu(CF$_3$)$_4$] (1.967(17) Å) [5]. The accuracy obtained in the geometry of the CF$_2$H groups has been limited by the large displacements of the C and F atoms (Fig. 4 and Table 8) — the mean C–F distance and F–C–F angle being 1.30(3) Å and 106(2)° respectively.

Since crystals of the CF$_3$ and CF$_2$H substituted cuprates are isomorphous, the relative orientation of the

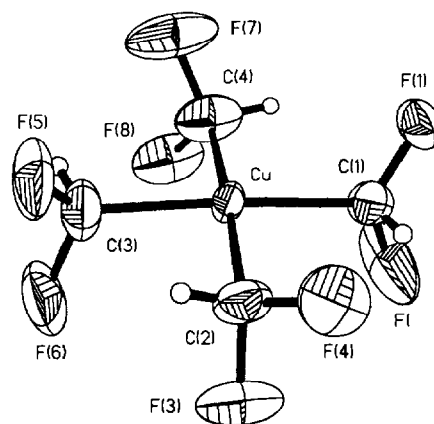Table 7
Selected bond lengths (Å) and angles (deg) for [PNP][Cu(CF$_2$H)$_4$]

Cu–C(1)	1.927(8)	Cu–C(3)	1.929(9)
Cu–C(2)	1.954(9)	Cu–C(4)	1.919(9)
F(1)–C(1)	1.268(10)	F(5)–C(3)	1.303(12)
F(2)–C(1)	1.265(12)	F(6)–C(3)	1.284(13)
F(3)–C(2)	1.343(10)	F(7)–C(4)	1.264(13)
F(4)–C(2)	1.310(11)	F(8)–C(4)	1.335(11)
C(4)–Cu–C(1)	92.1(6)	C(4)–Cu–C(3)	88.3(6)
C(1)–Cu–C(2)	91.0(5)	C(3)–Cu–C(2)	88.6(5)
C(1)–Cu–C(3)	175.7(5)	C(4)–Cu–C(2)	176.8(6)
F(2)–C(1)–F(1)	108.0(9)	F(6)–C(3)–F(5)	105.7(10)
F(2)–C(1)–Cu	111.9(8)	F(6)–C(3)–Cu	115.4(8)
F(1)–C(1)–Cu	122.4(6)	F(5)–C(3)–Cu	117.3(8)
F(4)–C(2)–F(3)	103.7(8)	F(7)–C(4)–F(8)	107.9(9)
F(4)–C(2)–Cu	119.3(7)	F(7)–C(4)–Cu	119.3(9)
F(3)–C(2)–Cu	110.7(7)	F(8)–C(4)–Cu	115.3(8)

Fig. 4. A perspective drawing of the [Cu(CF$_2$H)$_4$]$^\ominus$ anion in [PNP][Cu(CF$_2$H)$_4$] with 20% probability thermal ellipsoids for the non-hydrogen atoms.

CF$_3$ and CF$_2$H groups in these structures is of interest. The [Cu(CF$_3$)$_4$]$^\ominus$ anion was found to exhibit D_{2d} symmetry with one fluorine atom of each CF$_3$ group on a mirror plane. Such a structure minimizes F · · · F repulsions between CF$_3$ groups. A different rotamer is found for the CF$_2$H-substituted cuprate; that is, the CF$_2$H groups are rotated about their Cu–C bonds so as to approximate C_{4h} symmetry (Fig. 4). This structure maximizes the electrostatic interactions between H and F atoms of different CF$_2$H groups.

3. Experimental section

3.1. Reaction of R$_2$Cd with CF$_2$HI

(a) 2.5 g (14 mmol) CF$_2$HI [25] were condensed on 1.0 g (7 mmol) CdMe$_2$ dissolved in 2.5 ml diglyme. The mixture was stirred for 5 days at room temperature while the progress of the reaction was monitored by NMR spectroscopy. After evaporation of excess CF$_2$HI and separation from precipitated CdI$_2$, the reaction

mixture was treated with fresh (1.5 g, 10 mmol) CdMe$_2$ for 1 h. After NMR analysis, dimethylcadmium was removed in vacuo, and the mixture was re-analyzed by NMR.

(b) 2.0 g (12 mmol) CdEt$_2$ were dissolved in 1.7 ml (12 mmol) diglyme and stirred with 4.9 g (28 mmol) CF$_2$HI for 1 h at ambient temperature. After removal of

all volatile material in vacuo, 4.1 g of a colorless liquid was obtained which solidified to a glass at 10–15 °C.

3.2. Donor-free bis(difluoromethyl)cadmium, (CF$_2$H)$_2$Cd

7.2 g (40 mmol) of CF$_2$HI were stirred with 3.0 g (18 mmol) CdEt$_2$ in 8 ml CH$_2$Cl$_2$ for 30 min at

Table 8

Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [PNP][Cu(CF$_2$H)$_4$]

	x	y	z	$U_{(eq)}$ [a]
Cu	0.37304(8)	0.52954(8)	0.18932(2)	0.0635(2)
N	−0.1345(5)	1.1608(5)	0.02967(9)	0.0579(10)
P(1)	−0.02280(12)	1.23722(12)	0.00750(2)	0.0480(2)
P(2)	−0.20694(11)	1.18802(12)	0.06326(2)	0.0475(2)
F(1)	0.5863(5)	0.4699(7)	0.23450(14)	0.132(2)
F(2)	0.3903(10)	0.3881(15)	0.2445(3)	0.311(9)
F(3)	0.1400(7)	0.6425(7)	0.2186(2)	0.175(5)
F(4)	0.3188(8)	0.7594(8)	0.2312(2)	0.178(3)
F(5)	0.2963(9)	0.6865(8)	0.13579(15)	0.173(3)
F(6)	0.1455(9)	0.5396(13)	0.1488(2)	0.226(5)
F(7)	0.5603(9)	0.4022(8)	0.1473(3)	0.223(5)
F(8)	0.3926(8)	0.2673(6)	0.1601(2)	0.168(3)
C(1)	0.4544(9)	0.4881(16)	0.2306(2)	0.138(4)
C(2)	0.2654(9)	0.6873(11)	0.2073(2)	0.117(3)
C(3)	0.2795(13)	0.5626(14)	0.1490(2)	0.128(3)
C(4)	0.4730(13)	0.3760(11)	0.1695(4)	0.142(5)
C(11)	0.0765(5)	1.3738(5)	0.02658(10)	0.0520(10)
C(12)	0.0364(6)	1.5157(5)	0.02507(12)	0.0613(12)
C(13)	0.1098(7)	1.6155(6)	0.04268(13)	0.0712(15)
C(14)	0.2228(7)	1.5777(7)	0.06136(14)	0.0741(14)
C(15)	0.2613(6)	1.4394(7)	0.06367(15)	0.0743(14)
C(16)	0.1888(6)	1.3353(6)	0.04635(13)	0.0648(12)
C(21)	−0.1046(6)	1.3094(6)	−0.02774(11)	0.0596(12)
C(22)	−0.0283(8)	1.4001(7)	−0.04775(13)	0.076(2)
C(23)	−0.0889(10)	1.4444(8)	−0.0764(2)	0.096(2)
C(24)	−0.2919(10)	1.3081(11)	−0.0658(2)	0.110(3)
C(25)	−0.2198(12)	1.3952(10)	−0.0855(2)	0.110(3)
C(26)	−0.2367(7)	1.2634(7)	−0.03685(14)	0.077(2)
C(31)	0.0964(5)	1.1070(5)	−0.00789(11)	0.0540(10)
C(32)	0.0508(7)	0.9684(5)	−0.01157(13)	0.0659(13)
C(33)	0.1352(9)	0.8698(6)	−0.0274(2)	0.086(2)
C(34)	0.2651(9)	0.9097(8)	−0.0396(2)	0.092(2)
C(35)	0.3120(7)	1.0462(8)	−0.0355(2)	0.091(2)
C(36)	0.2293(6)	1.1449(7)	−0.02014(14)	0.0688(13)
C(41)	−0.3795(5)	1.1084(5)	0.06216(12)	0.0518(9)
C(42)	−0.4113(6)	1.0110(6)	0.03878(13)	0.0638(12)
C(43)	−0.5406(6)	0.9392(6)	0.0394(2)	0.078(2)
C(44)	−0.6340(6)	0.9662(6)	0.0630(2)	0.0735(14)
C(45)	−0.6048(6)	1.0630(7)	0.0869(2)	0.0742(15)
C(46)	−0.4765(5)	1.1364(6)	0.08678(12)	0.0597(11)
C(51)	−0.1159(5)	1.0962	0.09466(10)	0.0498(9)
C(52)	−0.0149(6)	0.9971(6)	0.08770(13)	0.0617(11)
C(53)	0.0476(7)	0.9159(7)	0.1114(2)	0.076(2)
C(54)	0.0092(7)	0.9352(7)	0.14288(15)	0.0748(15)
C(55)	−0.0919(7)	1.0357(7)	0.15055(13)	0.077(2)
C(56)	−0.1553(6)	1.1155(7)	0.12685(12)	0.0669(13)
C(61)	−0.2263(5)	1.3689(5)	0.07464(11)	0.0521(9)
C(62)	−0.1351(6)	1.4357(6)	0.09597(12)	0.0618(12)
C(63)	−0.1496(7)	1.5786(6)	0.10246(15)	0.0730(15)
C(64)	−0.2527(8)	1.6570(6)	0.0873(2)	0.081(2)
C(65)	−0.3421(7)	1.5932(6)	0.0661(2)	0.079(2)
C(66)	−0.3307(6)	1.4500(6)	0.05933(14)	0.0660(12)

[a] $U_{(eq)}$ is defined as one third of the trace of the U_{ij} tensor.

ambient temperature. Within 5 min a white precipitate was formed. After removal of CH_2Cl_2, EtI and excess CF_2HI in vacuo 3.8 g (18 mmol) of a white powder was obtained (*caution: $(CF_2H)_2Cd$ explodes violently when exposed to air or upon heating*). The identity was checked by NMR spectroscopy after dissolving in donor solvents as well by isolation and characterization as TMEDA and TMPDA complexes.

3.3. Adducts of bis(difluoromethyl)cadmium

As general procedure a slight excess of the ligand was added to donor-free $(CF_2H)_2Cd$ at -196 °C. After warming to room temperature excess ligand was removed in vacuo. In case of CH_3CN and dioxane, stoichiometric (1 : 2) quantities were required; prolonged pumping on these two complexes regenerates the starting material without decomposition. The TMEDA and TMPDA complexes were obtained quantitatively as white powders, which decompose slowly to CdF_2 in air. Combined DSC–TGA analyses show that the pathways of their thermal decomposition depend strongly on the heating rate. The major exothermic decomposition occurs at 70 and 142 °C respectively, with loss of the ligand and degradation of the CF_2H groups.

3.3.1. $(CF_2H)_2Cd \cdot TMEDA$

Anal. Found: C, 28.4; H 5.30; Cd, 33.9; F, 22.9; N, 8.1. $C_8H_{18}CdF_4N_2$. Calc.: C, 29.06; H, 5.49; Cd, 34.00; F, 22.98; N, 8.47%.

NMR (values in brackets are for the free donor), C_6D_6: $\delta(^{19}F)$ -118.9 ppm, $^2J(^{113/111}CdF)$ 222/212 Hz, $^4J(FF)$ 1.9 Hz, $\delta(CF_2^1H)$ 6.7 ppm, $^2J(HF)$ 43.0 Hz, $^2J(^{113/111}CdH)$ 89.8/85.8 Hz, $\delta(C^1H_3)$ 2.0 (2.1) ppm, $\delta(C^1H_2)$ 1.9 (2.3) ppm, $\delta(^{13}CF_2H)$ 148.9 ppm, $^1J(CF)$ 283.8 Hz, $^1J(^{113/111}Cd)$ 1119/1070 Hz, $^3J(CF)$ 6.1 Hz, $\delta(^{13}CH_3)$ 46.4 (45.8) ppm, $\delta(^{13}CH_2)$ 57.4 (58.2) ppm.

IR $(cm^{-1}$, KBr pellet): 3000 m, 2967 m, 2882/2856 s, 2809 m, 1470 s, 1357 w, 1293 s, 1252 w, 1189 w, 1167 w, 1132 m, 1069 vw, 1033 m, 1006 vs, 953 m, 894 vs, 790 s, 771 m, 581 w, 515 vw, 478 w, 437 m. Raman (cm^{-1}): 1479 s, 1442 w, 1418 vw, 1295 s, 1218 vw, 1138 vw, 1017 s, 930 m, 898 m, 780 s, 770 m, 516 s, 472 s, 445 m, 378 vw, 345 vw, 190 vs, 143 s.

3.3.2. $(CF_2H)_2Cd \cdot TMPDA$

Anal. Found: C, 31.1; H 5.70; Cd, 33.2; N, 7.8. $C_9H_{20}CdF_4N_2$. Calc.: C, 31.36; H, 5.85; Cd, 32.61; N, 8.13%. 1.183 g (3.43 mmol) of $(CF_2H)_2Cd \cdot TMPDA$ were hydrolyzed with diluted HNO_3 to yield 6.57 mmol CF_2H_2 (96.2%).

NMR (values in brackets are for the free donor), C_6D_6: $\delta(^{19}F)$ -118.4 ppm, $^2J(^{113/111}CdF)$ 214/204 Hz, $^4J(FF)$ 1.9 Hz, $\delta(CF_2^1H)$ 6.7 ppm, $^2J(HF)$ 42.9 Hz, $^2J(^{113/111}CdH)$ 90.3/86.5 Hz, $\delta(C^1H_3)$ 2.0 (2.1)

ppm, $\delta(NC^1H_2)$ 2.1 (2.2) ppm, $\delta(C^1H_2)$ 1.1 (1.5) ppm, $^3J(HH)$ 5.7 (7.2) Hz, $\delta(^{13}CF_2H)$ 149.0 ppm, $^1J(CF)$ 283.3 Hz, $^1J(^{113/111}CdC)$ 1111/1062 Hz, $^3J(CF)$ 6.6 Hz, $\delta(^{13}CH_3)$ 46.6 (45.4) ppm, $\delta(N^{13}CH_2)$ 60.5 (57.6) ppm, $\delta(^{13}CH_2)$ 23.5 (26.3) ppm.

IR $(cm^{-1}$, KBr pellet): 2963 m, 2846 s, 1477 s, 1287 s, 1247 w, 1234 w, 1201 w, 1185 m, 1041 m, 1004 vs, 967 m, 894 vs, 812 m, 738 m, 521 vw, 487 w, 461 w, 437 w.

3.4. Reaction of $(CF_2H)_2Cd$ with HCF_2I

A solution of 0.42 g (1.2 mmol) $(CF_2H)_2Cd \cdot$ diglyme in 0.5 ml diglyme was stirred with 0.7 g (4 mmol) HCF_2I at room temperature for 10 days. The conversion to the tetrafluoroethyl group was monitored by ^{19}F and ^1H NMR utilizing fluorobenzene (0.32 g) as an internal integration reference. A quantitative yield of $(HCF_2-CF_2)CdI$ and $(HCF_2CF_2)_2Cd$ (2 : 1 ratio) was obtained.

3.5. Transformation of $(CF_2H)_2Cd$ to $XCdCFHCl$

To a solution of 1.2 g (3.2 mmol) $(CF_2H)_2Cd \cdot$ diglyme in 1 ml diglyme 0.7 g (9 mmol) acetyl chloride (AcCl) were added. After stirring for 4 h at room temperature AcF, $AcCF_2H$ $AcCF_2Cl$, cis-, trans-1,2-difluoroethylene and excess AcCl were removed in vacuo, replaced by fresh AcCl and stirred for another 4 h. A final yield of 80% of CdCFHCl functions with a 1 : 1 ratio of (CFHCl)CdCl and $(CFHCl)_2Cd$ was determined spectroscopically by carrying out the reaction in the presence of fluorobenzene (0.55 g) as an internal integration reference.

3.6. Reaction of $(CF_2H)_2Cd$ with allyl bromide

A solution of 1.25 g (3.3 mmol) $(CF_2H)_2Cd \cdot$ diglyme in 2 ml diglyme was stirred with 0.38 g (3.2 mmol) allyl bromide for 5 h at room temperature. Fractional condensation gives $C_3H_5-CF_2H$ in 90–95% yield ($\delta(^{19}F)$ -116.8 ppm, $^2J(HF)$ 56.8 Hz, $^3J(HF)$ 17.8 Hz). If the reaction was carried out in the presence of one equivalent of CuCl at -30 °C, quantitative conversion was observed within 30 min.

3.7. Difluoromethylcopper derivatives

(a) A solution of 1.5 g (3.9 mmol) $(CF_2H)_2Cd \cdot$ diglyme and 0.77 g (7.8 mmol) CuCl in 1.5 ml diglyme was stirred for 10 min at -30 °C. After addition of 2 ml of a 1 : 1 mixture of HMPA and diglyme the solution was subjected to an NMR analysis showing the presence of $Cu(CF_2H)$. Warming this solution to 10 °C results in the formation of HF_2CCF_2H and cis / trans-1,2-difluoroethylene along with slow deposition of a solid material which consisted of elemental copper and

a residue, soluble in water or diluted HCl, containing copper, cadmium, fluoride and chloride ions. If the HMPA solution was exposed to oxygen, iodine or tetraethylthiuram disulfide at -20 °C only HF_2CCF_2H and CuX (X = I, 1/2O, $Et_2NC(S)S$) were observed.

(b) A solution of 1.0 g (2.8 mmol) $(CF_2H)_2Cd \cdot 2DMF$ in 2 ml DMF was stirred with 0.27 g (2.8 mmol) CuCl at -40 °C. After 10 min at -10 °C NMR analysis shows the conversion to $Cu(CF_2H)$ and $[Cu(CF_2H)_2]^\ominus$. Oxidation to Cu(III) was achieved either by bubbling dry air through the cold solution or by adding one equivalent of I_2 or tetraethylthiuram disulfide.

(c) Alternatively, 0.77 g (2.1 mmol) $(CF_2H)_2Cd \cdot 2DMF$ in 1 ml DMF were added to 1.5 g (4.0 mmol) $(Et_2NCS_2)Cu^{III}Br_2$ at -100 °C and warmed slowly to -60 °C. Upon melting, a yellow suspension was formed immediately which was warmed to ambient temperature, separated from the solid material and subjected to NMR analysis. Mixing this solution with that obtained according to procedure 3.7 (b) showed the identity of the copper species.

(d) $[PNP][Cu(CF_2H)_4]$ — to a solution of 2.25 g (10.5 mmol) $(CF_2)_2Cd$ in 6 ml DMF 1.04 g (10.5 mmol) CuCl were added at -30 °C in small portions. After stirring for 30 min the suspension was cooled to -60 °C. A solution of I_2 in DMF was added until the color of iodine persisted (2.6 g, 10.2 mmol I_2). After warming to room temperature the amount of the $[Cu(CF_2H)_4]$ anion being formed was determined by NMR spectroscopy, and an equimolar amount of [PNP]Cl (1.26 g, 2.2 mmol) was added. The solvent was removed at room temperature, and the residue treated with CH_2Cl_2. The extract was filtered, repeatedly washed with water, dried, and the solvent distilled off. Recrystallization from CH_2Cl_2–pentane yielded 835 mg (20%) $[PNP][Cu(CF_2H)_4]$ as colorless crystals.

Anal. Found: C, 59.6; H, 4.25; Cu, 8.1; F, 18.9, N, 1.67. $C_{40}H_{34}CuF_8NP_2$. Calc.: C, 59.59; H, 4.40; Cu, 7.88; F, 18.85; N, 1.74%.

IR $(cm^{-1}$, KBr pellet): 3059 m, 2922 s, 1482 m, 1438 s, 1315 w, 1295 m, 1264 vs, 1186 m, 1120 s, 1000 vs, 944 vs, 803 m, 758 w, 753 m, 748 m, 741 m, 729 sh, 722 s, 699 sh, 691 s, 666 vw, 627 w, 550 vs, 536 vs, 526 m, 498 s, 458 vw. Raman (cm^{-1}): 3072 m, 2945 m, 1592 s, 1578 m, 1270 m, 1189 m, 1167 m, 1116 s, 1036 s, 1004 vs, 752 w, 661 s, 632 m, 618 s, 606 vs, 596 sh, 540 m, 532 m, 236 s, 200 w, 171 w, 81 vs, 42 m.

3.8. Difluoromethyl(trifluoromethyl)cuprates(III)

To a solution of 1.2 mmol of $(CF_3)_2Cu^{III}(S_2CNEt_2)$ [4] $(\delta(^{19}F)$ -30.7 ppm) in 1.5 ml DMF, prepared by reaction of $(Et_2NCS_2)Cu^{III}Br_2$ with $(CF_3)_2Cd \cdot$ diglyme, 1.2 mmol $(CF_2H)_2Cd \cdot 2$ DMF were added at -50 °C.

After 5 min at ambient temperature, one equivalent of [PNP]Cl was added, and the solvent was removed. Extraction with $CHCl_3$ followed by removal of the solvent gave a yellow material which dissolved with red color in $CHCl_3$ and showed the presence of mixed CF_3/CF_2H species by NMR analysis.

3.9. X-ray structure determination

A crystal of $[PNP][Cu(CF_2H)_4]$, which was grown by slow diffusion of pentane into a CH_2Cl_2 solution, having the dimensions $0.28 \times 0.32 \times 0.50$ mm^3 was mounted in a glass capillary under argon. X-ray measurements were made at 297 K with a Siemens P3 diffractometer using graphite monochromatized Cu K α (λ 1.54184 Å) radiation. The crystal belongs to the tetragonal space group $P4_1$ with $a = 9.443(1)$ Å, $c = 41.803(5)$ Å, $Z = 4$, $D_c = 1.436$ g cm^{-3}. Using 2θ–ω scans $(2\theta < 138.2°)$ a total of 4072 reflections were measured — 3535 being unique. The data were corrected for the drift of the three periodically measured monitor reflections and empirically for absorption as detected by ψ scans. The structure was solved by direct methods and refined on F^2 using all unique reflections (SHELXTL). Hydrogen atoms were placed in idealized positions (C–H 0.95 Å) with an appropriate riding model. The refinement of the 477 parameters, which included an extinction correction of the form $F_c^* = F_c(1 + x\lambda^3 F_c^2/\sin2\theta)^{-1/4}$ where $x = 2.0(2) \times 10^{-6}$, converged with $R_F = 0.041$ for the 3333 observed reflections $(F_o > 4\sigma(F_o))$ and $wR_F^2 = 0.115$ for all reflections. The final coordinates of the non-hydrogen atoms are listed in Table 8. Additional crystallographic details may be obtained from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein–Leopoldshafen, by quoting the deposit number CSD-405185, the names of the authors and the literature reference.

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