

Preliminary communication

Donor-free bis(trifluoromethyl) cadmium, $(\text{CF}_3)_2\text{Cd}$: a readily available low-temperature difluorocarbene source

R. Eujen *, B. Hoge

Anorganische Chemie, Fachbereich 9, Universität-GH, 42097 Wuppertal, Germany

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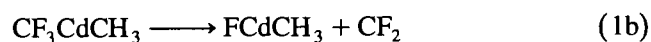
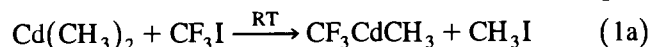
Abstract

Donor-free bis(trifluoromethyl)cadmium, $(\text{CF}_3)_2\text{Cd}$, has been obtained at -40°C from diethylcadmium and CF_3I in a quantitative yield. The Raman spectrum of $(\text{CF}_3)_2\text{Cd}$ is reported. In the presence of non-coordinating solvents the highly reactive compound eliminates CF_2 even below -5°C . Its feasibility as a low temperature difluorocarbene source has been demonstrated by difluorocyclopropanation reactions with some alkenes and alkynes as well as by insertion into metal–chlorine bonds. The NMR spectra of some CF_2Cl - and CF_3 -containing arsanes are reported.

Keywords: Cadmium; Arsenic; Difluorocarbene; Trifluoromethyl

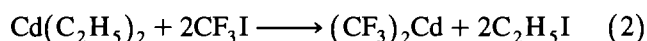
Donor-stabilized bis(trifluoromethyl)cadmium $((\text{CF}_3)_2\text{Cd} \cdot 2\text{D})$ is well known. In these complexes the Lewis acidity of the tetracoordinated cadmium atom is reduced by the donor, which is typically an ether such as mono- or diglyme, CH_3CN , pyridine or DMF [1]. Prepared readily by CH_3/CF_3 exchange between CdMe_2 and CF_3I in the presence of a donor [2] it has found valuable applications both as a trifluoromethylating agent [3] and as a difluorocarbene source [4,5]. Unstable, donor-free $(\text{CF}_3)_2\text{Cd}$ has been obtained by cocondensation of cadmium vapor and CF_3 radicals generated in a r.f. discharge [6] and characterized by its ^{19}F NMR spectrum utilizing CD_2Cl_2 as solvent.

We have reinvestigated the alkyl group exchange and found that in the solvent-free system one CH_3 group of CdMe_2 is exchanged by CF_3I within 5 min at 20°C . The resulting CF_3CdCH_3 does not undergo further exchange with CF_3I but decomposes to the fluoride and difluorocarbene, which forms C_2F_4 and $c\text{-C}_3\text{F}_6$ and also inserts into a cadmium–carbon bond of CdMe_2 :



Details of these and related Cd–C insertion reactions and products will be described elsewhere [7].

The reactivity of CdEt_2 towards exchange with CF_3I is much higher than that of CdMe_2 which allows the lowering of the reaction temperature. If CF_3I is reacted with CdEt_2 (molar ratio 2.5:1) in chloroform at -40°C the exchange according to



is complete within 10 min and $(\text{CF}_3)_2\text{Cd}$ precipitates quantitatively as a white powder. Solvent, excess CF_3I and $\text{C}_2\text{H}_5\text{I}$ are removed in vacuo. Above -5°C $(\text{CF}_3)_2\text{Cd}$ decomposes to CdF_2 and CF_2 , the latter

Table 1
Solid state Raman spectra ^a of polycrystalline $(\text{CF}_3)_2\text{Cd}$ ^b and $(\text{CF}_3)_2\text{Hg}$ [8]

$(\text{CF}_3)_2\text{Cd}$	$(\text{CF}_3)_2\text{Hg}$	Assignment
196 s	224 vs	$\left. \begin{matrix} a_g \\ f_g \end{matrix} \right\} \nu_s (\text{MC})$
218 m-s	234 s	
–	516 w	$\delta_{as} (\text{CF}_3)$
696 s	714 s	$\delta_s (\text{CF}_3)$
960 sh	1030 w	} $\nu_{as} (\text{CF}_3)$
980 m, b	1043 m	
1135 sh	1146 m	$\left. \begin{matrix} a_g \\ f_g \end{matrix} \right\} \nu_s (\text{CF}_3)$
1157 s	1163 s	

^a In cm^{-1} ; s strong, m medium, w weak, v very, sh shoulder, b broad.

^b Recorded at -50°C .

* Corresponding author.

oligomerizing to the volatile products C_2F_4 and $c-C_3F_6$ (Warning: Pure $(CF_3)_2Cd$ tends to explode violently upon warming to room temperature!). The reaction with donor molecules leads to the known adducts but may proceed so exothermically that some decomposition takes place. $(CF_3)_2Cd$ reacts pyrophorically with air.

The Raman spectrum of solid $(CF_3)_2Cd$ recorded at $-50^\circ C$ (Table 1) strongly resembles that of $(CF_3)_2Hg$ [8], especially in that there are two intense $\nu(CdC)$ modes which have been assigned to the a_g/f_g crystal field components of the a_{1g} vibration. In accord with a very weak Cd–C bond this mode which is independent

of the metal mass appears at lower energy than that of $(CF_3)_2Hg$. Furthermore, the significant red-shift especially of the $\nu_{as}(CF_3)$ stretch, along with the non-volatility of $(CF_3)_2Cd$, points towards an increased strength of intermolecular fluorine contacts to the more Lewis-acidic cadmium atom which again favor the release of CF_2 . Weak Hg–F contacts have also been found for $(CF_3)_2Hg$ [8] which in contrast to the non-volatile $(CF_3)_2Cd$ sublimes even below ambient temperature.

The stability of $(CF_3)_2Cd$ is readily controlled by the solvent. In solvents of low polarity such as $CHCl_3$, CH_2Cl_2 or toluene it decomposes quantitatively even

Table 2
Difluorocarbene cyclopropanation products ^a

Educt	Product	¹⁹ F NMR	Ref.
cyclohexene		– 150.6 ppm (d), ² J(FF) 155.6 Hz – 125.9 ppm (d, t), ³ J(FH) 15.3 Hz	[9]
1-hexene		– 145.3 ppm (d, d), ² J(FF) 155.9 Hz, ³ J(FH) 13.1 Hz, – 128.4 ppm (d, t), ³ J(FH) 13.1 Hz	[10]
2,3-dimethyl-2-butadiene ^b		– 137.4 ppm ^c (t, q), ³ J(FH _{cis} + FH _{tr}) 16.0/15.6 Hz, ⁴ J(F _A H + F _B H) 4.5 Hz	
trans-butene		– 141.7 ppm, ² J(FF) 154.0 Hz, ³ J(HF _{cis}) 16.0 Hz, ³ J(HF _{tr}) 0.8 Hz, ⁴ J(HF _{cis}) 2.9 Hz, ⁴ J(HF _{tr}) 1.6 Hz	[9,10]
cis-stilbene ^d		– 147.0 ppm (d), ² J(FF) 157.2 Hz, – 117.2 ppm (d, t), ³ J(FH) 14.3 Hz	
trans-stilbene		– 134.0 ppm (t), ³ J(FH _{cis} + FH _{tr}) 15.2 Hz	
cyclohexylacetylene		– 103.2 ppm (d, d), ⁴ J(FH) 2.6 Hz, ³ J(FH) 1.7 Hz	[11]
diphenylacetylene		– 112.3 ppm (s)	

^a In toluene. Yields as determined by ¹⁹F NMR spectroscopy are in excess of 95%. ¹⁹F NMR chemical shifts are given with reference to external $CFCl_3$; multiplicities from proton coupled spectra are indicated s singlet, d doublet, t triplet, q quartet.

^b With an excess of $Cd(CF_3)_2$ addition of a second CF_2 moiety with formation of two isomers (ratio I:II = 4:1) is observed. Isomer (I): $\delta(^{19}F)$ – 137.7 ppm (F_A), – 139.3 ppm (F_B), ²J(FF) 156.8 Hz, ⁵J($F_A F_B'$) 2.5 Hz, ⁵J($F_B F_B'$) 1.9 Hz, ⁵J($F_A F_A'$) 1.3 Hz; Isomer (II): $\delta(^{19}F)$ – 135.0 ppm (F_A), – 139.9 ppm (F_B); ²J(FF) 159.0 Hz, ⁵J($F_A F_B'$) 1.3 Hz, ⁵J($F_B F_B'$) 1.8 Hz, ⁵J($F_A F_A'$) 0.4 Hz.

^c $\delta(F_A) - \delta(F_B) \approx 0.02$ ppm.

^d In chloroform.

Table 3
NMR data of the products from the reaction of $\text{Cd}(\text{CF}_3)_2$ with AsCl_3 or AsF_3 ^a

	$\delta(^{19}\text{F})$ ^b		$\delta(^{19}\text{F})$	$\delta(^{13}\text{C})$	$^1J(\text{CF})$	$^2J(\text{CF})$	$^3J(\text{CF})$	$^2J(\text{FF})$	$^3J(\text{FF})$	$^4J(\text{FF})$
	(CF_2Cl)	$\Delta\delta(\text{F}_A - \text{F}_B)$	(CF_3)	(CF_3 or CF_2Cl)						
$\text{As}(\text{CF}_3)_3$	–	–	–47.1 ^d	127.4	340.6 ^e	–	4.7 ^e	–	–	7.1 ^e
$\text{As}(\text{CF}_3)_2\text{Cl}$	–	–	–56.4	127.7	345.3	–	6.0	–	–	7.8
$\text{As}(\text{CF}_3)_2\text{F}$	–	–	–59.8	129.6	344.5	^c	6.0	–	1.4	7.3
$\text{As}(\text{CF}_3)\text{Cl}_2$	–	–	–65.8	128.8	349.5	–	–	–	–	–
$\text{As}(\text{CF}_3)\text{F}_2$ ^f	–	–	–71.0	131.0	346.1	^c	–	–	1.7	–
$\text{As}(\text{CF}_3)_2(\text{CF}_2\text{Cl})$	–41.6	–	–46.4	^c	^c	–	^c	–	–	7.5
$\text{As}(\text{CF}_3)(\text{CF}_2\text{Cl})_2$	–41.8	0.22	–46.6	^c	^c	–	^c	^c	–	7.0 ^g
$\text{As}(\text{CF}_2\text{Cl})_2\text{Cl}$	–49.6	1.00	–	130.0	^c	–	^c	158.5	–	8.7 ^h
$\text{As}(\text{CF}_2\text{Cl})_2\text{F}$	–53.5	0.94	–	^c	^c	–	^c	165.9	6.6/5.5	8.9 ⁱ
$\text{As}(\text{CF}_2\text{Cl})\text{Cl}_2$	–57.9	–	–	131.9	355.2	–	–	–	–	–
$\text{As}(\text{CF}_2\text{Cl})\text{FCl}$	–61.4	≈ 0.0	–	133.7	353.1	18.7	–	–	4.0	–
$\text{As}(\text{CF}_2\text{Cl})\text{F}_2$ ^j	–65.2	–	–	134.9	350.7	17.5	–	–	1.4	–

^a Chemical shifts in ppm with reference to external CFCl_3 , coupling constants in Hz, solvent: CDCl_3 .

^b Averaged values for AB systems.

^c Not observed.

^d $\Delta\delta(^{12}\text{C F}_A - ^{13}\text{C F}_B)$ 0.137 ppm.

^e Positive signs for both $^3J(\text{CF})$ and $^4J(\text{FF})$ have been determined with respect to the negative sign of $^1J(\text{CF})$ by computer simulation of the $\text{A}_3\text{B}_6\text{X}$ spin system.

^f $\delta(\text{As F})$ – 118.0 ppm (broad).

^g $[\text{AB}]_2\text{X}_3$ system, $^4J(\text{AA}') \approx ^4J(\text{BB}') \approx ^4J(\text{AB}') 7.0$ Hz; $^4J(\text{AX}) \approx ^4J(\text{BX}) 7.3$ Hz.

^h $^4J(\text{AA}')$; $^4J(\text{AB}')$ 9.4 Hz, $^4J(\text{BB}')$ 9.7 Hz.

ⁱ $^4J(\text{AA}') \approx ^4J(\text{BB}')$; $^4J(\text{AB}') = 9.8$ Hz.

^j $\delta(\text{As}^{19}\text{F})$ – 111.2 ppm (broad).

below -5°C with evolution of CF_2 which may be trapped quantitatively with electron rich unsaturated systems. A selection of difluorocyclopropanation reactions along with characteristic NMR data is given in Table 2. With electron-poor systems such as allyl bromide dimerization of CF_2 is preferred, and only minor amounts of (bromomethyl)difluorocyclopropane have been detected by NMR spectroscopy ($\delta(^{19}\text{F})$ – 127.6/– 144.9 ppm, $^1J(\text{FF})$ 159.4 Hz). The synthetic potential of the cadmium reagent was also used

for the generation of difluoromethyl ethers from alcohols. For example, when *i*-propanol and a suspension of excess $(\text{CF}_3)_2\text{Cd}$ in toluene were slowly warmed from -30°C to ambient temperature, $(\text{CH}_3)_2\text{CHO CF}_2\text{H}$ ($\delta(^{19}\text{F})$ – 81.7 ppm, $^2J(\text{FH})$ 77.6 Hz) [12] was obtained in 50% yield along with HCF_3 .

With inorganic chlorides such as Me_3SnCl or AsCl_3 insertion of CF_2 into the metal–halide bond with formation of CF_2Cl derivatives along with some trifluoromethylation is observed. Presumably, the latter is due

Table 4
NMR data of compounds observed in the reaction of $\text{Cd}(\text{CF}_3)_2$ with AsCl_3 or AsF_3 in presence of CdEt_2 ^a

	$\delta(^{19}\text{F})$ ^b		$\delta(^{19}\text{F})$	$^2J(\text{FF})$	$^4J(\text{FF})$	$^4J(\text{HF})$	$^5J(\text{HF})$
	(CF_2Cl)	$\Delta\delta(\text{F}_A - \text{F}_B)$	(CF_3)	(CF_3 or CF_2Cl)			
$\text{As}(\text{CF}_2\text{Cl})_2\text{Et}$	–44.5	1.13	–	163.4	8.0 ^d	^c	0.9/0.4
$\text{As}(\text{CF}_2\text{Cl})\text{Et}_2$ ^c	–44.0	–	–	–	–	0.4	0.9
$\text{As}(\text{CF}_2\text{Cl})(\text{F})\text{Et}$ ^f	–56.4	1.60	–	162.1	–	^c	0.9/0.6
$\text{As}(\text{CF}_2\text{Cl})(\text{Cl})\text{Et}$	–52.8	1.96	–	156.9	–	^c	1.3 ^g
$\text{As}(\text{CF}_3)\text{Et}_2$	–	–	–53.1	–	–	^c	0.7
$\text{As}(\text{CF}_3)(\text{Cl})\text{Et}$	–	–	–50.2	–	–	0.3	0.7
$\text{As}(\text{CF}_3)(\text{CF}_2\text{Cl})\text{Et}$	–44.5	1.05	–50.6	164.6	6.9 ^h	^c	0.7 ⁱ

^a See Table 3.

^b Averaged values for AB systems.

^c Not observed.

^d $^4J(\text{AA}')$; $^4J(\text{AB}')$ 7.3 Hz; $^4J(\text{BB}')$ 6.5 Hz.

^e $\delta(\text{CH}_3)$ 1.2 ppm, $^3J(\text{HH})$ 7.8 Hz, $\delta(\text{CH}_2)$: (AB system) 1.9/1.7 ppm, $^2J(\text{HH})$ 13.1 Hz, $\delta(^{13}\text{CF}_2\text{Cl})$ 133.2 ppm, $^1J(\text{CF})$ 346.5 Hz, $^3J(\text{CH})$ 5.0 Hz.

^f $^3J(\text{F}_A\text{F})$ 8.4 Hz, $^3J(\text{F}_B\text{F})$ 4.2 Hz.

^g $^5J(\text{F}_A\text{H})$; $^5J(\text{F}_B\text{H})$ 0.7 Hz.

^h $^4J(\text{F}_A\text{F}) \approx ^4J(\text{F}_B\text{F})$.

ⁱ $^5J(\text{CF}_3\text{AsCH}_2\text{CH}_3)$.

to fluorination by the cadmium fluoride formed in the course of the reaction followed by insertion of CF_2 into the M–F bond. For example, the reaction of Me_3SnCl with $(\text{CF}_3)_2\text{Cd}$ in CHCl_3 gives both $(\text{CF}_2\text{Cl})\text{SnMe}_3$ ($\delta(^{19}\text{F}) -46.6$ ppm, $^2J(^{119/117}\text{SnF})$ 236.2/225.7 Hz, $\Delta\delta(^{35}\text{Cl}-^{37}\text{Cl})$ 0.0096 ppm) and CF_3SnMe_3 in a 2:1 ratio with a total yield of 90%. With AsCl_3 the distribution of the products seems to be similar to that of the reaction of donor-stabilized $(\text{CF}_3)_2\text{Cd}$ [5]. The formation of $(\text{CF}_2\text{Cl})\text{AsX}_2$ ($\text{X} = \text{F}, \text{Cl}$) along with mixed $\text{CF}_3/\text{CF}_2\text{Cl}$ containing species $(\text{CF}_3)_n(\text{CF}_2\text{Cl})_m\text{AsX}_{3-n-m}$ is evident from the ^{19}F NMR spectra (Table 3), the CF_2Cl function being easily recognized by its isotope pattern in the ^{19}F NMR spectra ($\Delta\delta(^{35}\text{Cl}-^{37}\text{Cl})$ 0.006 ppm). The facile insertion of CF_2 into the As–F bond was independently demonstrated by reaction of AsF_3 with excess $(\text{CF}_3)_2\text{Cd}$ which yields $(\text{CF}_3)_3\text{As}$ almost quantitatively. If the reaction is carried out with a material still containing residual CdC_2H_5 functions, partial ethylation of the products is observed (Table 4) with $(\text{CF}_2\text{Cl})\text{AsEt}_2$ as the major product.

Acknowledgements

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