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Preliminary communication

Donor-free bis(trifluoromethyl)cadmium, $(CF_3)_2Cd$: a readily available low-temperature difluorocarbene source

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Abstract

Donor-free bis(trifluoromethyl)cadmium, $(CF_3)_2Cd$, has been obtained at −40 °C from diethylcadmium and CF_3I in a quantitative yield. The Raman spectrum of $(CF_3)_2Cd$ 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 difluorocyclopropenation 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 ($(CF_3)_2Cd \cdot 2$ 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 $(CF_3)_2Cd$ 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 $c\text{-}C_3F_6$ and also inserts into a cadmium–carbon bond of $CdMe_2$:

$$Cd(CH_3)_2 + CF_3I \xrightarrow{RT} CF_3CdCH_3 + CH_3I \quad (1a)$$

$$CF_3CdCH_3 \longrightarrow FCdCH_3 + CF_2 \quad (1b)$$

$$CH_3CdCH_3 + CF_2 \longrightarrow CH_3CdCF_2CH_3 \quad (1c)$$

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

$$Cd(C_2H_5)_2 + 2CF_3I \longrightarrow (CF_3)_2Cd + 2C_2H_5I \quad (2)$$

is complete within 10 min and $(CF_3)_2Cd$ precipitates quantitatively as a white powder. Solvent, excess CF_3I and C_2H_5I are removed in vacuo. Above −5 °C $(CF_3)_2Cd$ decomposes to CdF_2 and CF_2, the latter

Table 1
Solid state Raman spectra [a] of polycrystalline $(CF_3)_2Cd$ [b] and $(CF_3)_2Hg$ [8]

$(CF_3)_2Cd$	$(CF_3)_2Hg$	Assignment	
196 s	224 vs	a_g	ν_s (MC)
218 m–s	234 s	f_g	
–	516 w		δ_{as} (CF_3)
696 s	714 s		δ_s (CF_3)
960 sh	1030 w		ν_{as} (CF_3)
980 m, b	1043 m		
1135 sh	1146 m	a_g	ν_s (CF_3)
1157 s	1163 s	f_g	

[a] In cm^{-1}; s strong, m medium, w weak, v very, sh shoulder, b broad.
[b] Recorded at −50°C.

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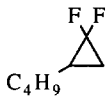
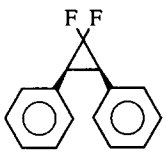
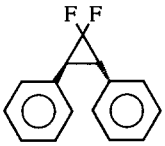
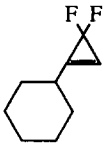
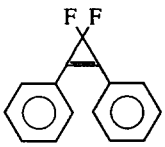
oligomerizing to the volatile products C_2F_4 and c-C_3F_6 (Warning: *Pure $(CF_3)_2Cd$ tends to explode violently upon warming to room temperature!).* The reaction with donor molecules leads to the known adducts but may proceed so exothermically that some decompositon takes place. $(CF_3)_2Cd$ reacts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

The Raman spectrum of solid $(CF_3)_2Cd$ recorded at −50 °C (Table 1) strongly resembles that of $(CF_3)_2Hg$ [8], especially in that there are two intense ν(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 cyclopropenation products [a]

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

[a] In toluene. Yields as determined by ^{19}F NMR spectroscopy are in excess of 95%. ^{19}F 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, $^5J(F_AF_{B'})$ 2.5 Hz, $^5J(F_BF_{B'})$ 1.9 Hz, $^5J(F_AF_{A'})$ 1.3 Hz; Isomer (II): $\delta(^{19}F)$ −135.0 ppm (F_A), −139.9 ppm (F_B); ^2J(FF) 159.0 Hz, $^5J(F_AF_{B'})$ 1.3 Hz, $^5J(F_BF_{B'})$ 1.8 Hz, $^5J(F_AF_{A'})$ 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 $Cd(CF_3)_2$ with $AsCl_3$ or AsF_3 [a]

	$\delta(^{19}F)$ [b]		$\delta(^{19}F)$	$\delta(^{13}C)$	$^1J(CF)$	$^2J(CF)$	$^3J(CF)$	$^2J(FF)$	$^3J(FF)$	$^4J(FF)$
	(CF_2Cl)	$\Delta\delta(F_A - F_B)$	(CF_3)	$(CF_3$ or $CF_2Cl)$						
$As(CF_3)_3$	–	–	−47.1 [d]	127.4	340.6 [e]	–	4.7 [e]	–	–	7.1 [e]
$As(CF_3)_2Cl$	–	–	−56.4	127.7	345.3	–	6.0	–	–	7.8
$As(CF_3)_2F$	–	–	−59.8	129.6	344.5	[c]	6.0	–	1.4	7.3
$As(CF_3)Cl_2$	–	–	−65.8	128.8	349.5	–	–	–	–	–
$As(CF_3)F_2$ [f]	–	–	−71.0	131.0	346.1	[c]	–	–	1.7	–
$As(CF_3)_2(CF_2Cl)$	−41.6	–	−46.4	[c]	[c]	–	[c]	–	–	7.5
$As(CF_3)(CF_2Cl)_2$	−41.8	0.22	−46.6	[c]	[c]	–	[c]	[c]	–	7.0 [g]
$As(CF_2Cl)_2Cl$	−49.6	1.00	–	130.0	[c]	–	[c]	158.5	–	8.7 [h]
$As(CF_2Cl)_2F$	−53.5	0.94	–	[c]	[c]	–	[c]	165.9	6.6/5.5	8.9 [i]
$As(CF_2Cl)Cl_2$	−57.9	–	–	131.9	355.2	–	–	–	–	–
$As(CF_2Cl)FCl$	−61.4	≈ 0.0	–	133.7	353.1	18.7	–	–	4.0	–
$As(CF_2Cl)F_2$ [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] $\Delta\delta(^{12}CF_A - ^{13}CF_B)$ 0.137 ppm.
[e] Positive signs for both $^3J(CF)$ and $^4J(FF)$ have been determined with respect to the negative sign of $^1J(CF)$ by computer simulation of the A_3B_6X spin system.
[f] $\delta(AsF) - 118.0$ ppm (broad).
[g] $[AB]_2X_3$ system, $^4J(AA') \approx {}^4J(BB') \approx {}^4J(AB')$ 7.0 Hz; $^4J(AX) \approx {}^4J(BX)$ 7.3 Hz.
[h] $^4J(AA')$; $^4J(AB')$ 9.4 Hz, $^4J(BB')$ 9.7 Hz.
[i] $^4J(AA') \approx {}^4J(BB')$; $^4J(AB') = 9.8$ Hz.
[j] $\delta(As^{19}F) - 111.2$ ppm (broad).

below −5 °C with evolution of CF_2 which may be trapped quantitatively with electron rich unsaturated systems. A selection of difluorocyclopropenation 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 (δ (^{19}F) −127.6/−144.9 ppm, $^1J(FF)$ 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 $(CF_3)_2Cd$ in toluene were slowly warmed from −30 °C to ambient temperature, $(CH_3)_2CHOCF_2H$ ($\delta(^{19}F)$ −81.7 ppm, $^2J(FH)$ 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 $Cd(CF_3)_2$ with $AsCl_3$ or AsF_3 in presence of $CdEt_2$ [a]

	$\delta(^{19}F)$ [b]		$\delta(^{19}F)$	$^2J(FF)$	$^4J(FF)$	$^4J(HF)$	$^5J(HF)$
	(CF_2Cl)	$\Delta\delta(F_A - F_B)$	(CF_3)	$(CF_3$ or $CF_2Cl)$			
$As(CF_2Cl)_2Et$	−44.5	1.13	–	163.4	8.0 [d]	[c]	0.9/0.4
$As(CF_2Cl)Et_2$ [c]	−44.0	–	–	–	–	0.4	0.9
$As(CF_2Cl)(F)Et$ [f]	−56.4	1.60	–	162.1	–	[c]	0.9/0.6
$As(CF_2Cl)(Cl)Et$	−52.8	1.96	–	156.9	–	[c]	1.3 [g]
$As(CF_3)Et_2$	–	–	−53.1	–	–	[c]	0.7
$As(CF_3)(Cl)Et$	–	–	−50.2	–	–	0.3	0.7
$As(CF_3)(CF_2Cl)Et$	−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] $^4J(AA')$; $^4J(AB')$ 7.3 Hz; $^4J(BB')$ 6.5 Hz.
[e] $\delta(CH_3)$ 1.2 ppm, $^3J(HH)$ 7.8 Hz, $\delta(CH_2)$: (AB system) 1.9/1.7 ppm, $^2J(HH)$ 13.1 Hz, $\delta(^{13}CF_2Cl)$ 133.2 ppm, $^1J(CF)$ 346.5 Hz, $^3J(CH)$ 5.0 Hz.
[f] $^3J(F_AF)$ 8.4 Hz, $^3J(F_BF)$ 4.2 Hz.
[g] $^5J(F_AH)$; $^5J(F_BH)$ 0.7 Hz.
[h] $^4J(F_AF) \approx {}^4J(F_BF)$.
[i] $^5J(CF_3AsCH_2CH_3)$.

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 $(CF_3)_2Cd$ in $CHCl_3$ gives both $(CF_2Cl)SnMe_3$ ($\delta(^{19}F)$ −46.6 ppm, $^2J(^{119/117}SnF)$ 236.2/225.7 Hz, $\Delta\delta(^{35}Cl\text{-}^{37}Cl)$ 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 $(CF_3)_2Cd$ [5]. The formation of $(CF_2Cl)AsX_2$ (X = F, Cl) along with mixed CF_3/CF_2Cl containing species $(CF_3)_n(CF_2Cl)_mAsX_{3-n-m}$ 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 ($\Delta\delta(^{35}Cl\text{-}^{37}Cl)$ 0.006 ppm). The facile insertion of CF_2 into the As–F bond was independently demonstrated by reaction of AsF_3 with excess $(CF_3)_2Cd$ which yields $(CF_3)_3As$ 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 $(CF_2Cl)AsEt_2$ as the major product.

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