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The chemistry of poly(trifluoromethyl)benzenes: unusual reactions of 1,2,4,5-tetrakis(trifluoromethyl)benzene with organolithium compounds*[†]

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Abstract

1,2,4,5-Tetrakis(trifluoromethyl)benzene reacts with alkyl- or aryl-lithium compounds in an unexpected way. Instead of lithiation of the aromatic ring, dearomatisation occurs to give 2,5-cyclohexadiene-1-ylidene derivatives of the general formula $C_{10}H_2F_{10}R_2$, where R = alkyl or aryl. The X-ray and NMR analyses gave unequivocal proof of the structure of the products.

Introduction

The chemistry of poly(trifluoromethyl)benzenes, in spite of the relative accessibility of these compounds, has received only limited attention. A long time ago, it was reported that treatment of hexakis(trifluoromethyl)benzene with potassium hydroxide in an ethanol–water solution at room temperature results in the hydrolysis of the trifluoromethyl groups to give ethyl pentakis(trifluoromethyl)benzoate [1]. The reaction with methanolic sodium methoxide proceeds readily at 0 °C to give the *ortho* ester in a 92% isolable yield. Acidic hydrolysis of the *ortho* ester affords, almost quantitatively, methyl pentakis(trifluoromethyl)benzoate [2]. Tetrakis-, pentakis- and hexakis-(trifluoromethyl)benzenes were reported to react readily with liquid ammonia at ambient temperature to give, respectively, 2,4,6-tricyanobenzotrifluoride, 1,2,4-tris-(trifluoromethyl)-3,5-dicyanobenzene and 1,3,5-tris-(trifluoromethyl)-2,4,6-tricyanobenzene [3].

Another type of reactivity of poly(trifluoromethyl)benzenes, previously reported, is lithiation of the benzene ring. Such lithiation proceeds predominantly or exclusively at the position *ortho* to a trifluoromethyl group. Yields of the corresponding lithium derivatives drastically decrease with increasing

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*Dedicated to Prof. Dr Mult. Alois Haas on his 60th birthday in appreciation of his contribution to fluorine chemistry.

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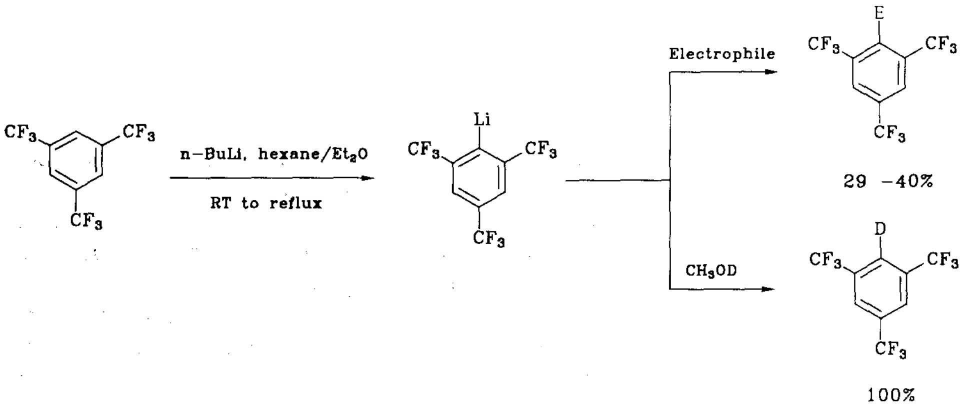
crowding at the benzene ring. Thus, lithiation of benzotrifluoride [4] and 1,2-bis(trifluoromethyl)benzene [5], followed by carboxylation, resulted in 48% and 40% yields of mono- and bis-(trifluoromethyl)benzoic acids, respectively, while from 1,2,3-tris(trifluoromethyl)benzene [5] the respective acid was obtained in only 9% yield. Lithiation of 1,3-bis(trifluoromethyl)-benzene gives a 1:3 mixture of 2,6- and 2,4-bis(trifluoromethyl)phenyl-lithium, as determined from the ratio of products of the consecutive reaction with chlorodifluorophosphine [6]. However, in the presence of tetramethyl-ethylenediamine (TMEDA), the lithiation occurs exclusively at the most active position between the two trifluoromethyl groups to give 2,6-bis(trifluoromethyl)phenyl-lithium as the sole product [7].

Chambers *et al.* [8] reported that 1,3,5-tris(trifluoromethyl)benzene reacts with butyl-lithium at room temperature to form remarkably thermally stable 2,4,6-tris(trifluoromethyl)phenyl-lithium, which reacts with a variety of electrophiles in a conventional fashion to give reasonable to good yields of functionalised derivatives. The hydrogen–lithium exchange is essentially quantitative, as established by quenching with deuteriomethanol and subsequent mass-spectroscopic examination of the recovered material.

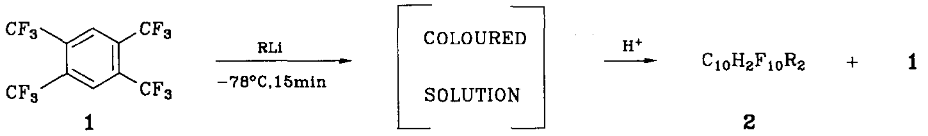


Scheme 1.

That work prompted us to undertake a study of the lithiation of other poly(trifluoromethyl)benzenes. The present work describes unexpected reactions of 1,2,4,5-tetrakis(trifluoromethyl)benzene (**1**) with alkyl- and phenyl-lithium reagents.

Results and discussion

In contrast to 1,3,5-tris(trifluoromethyl)benzene [8], attempted lithiation of 1,2,4,5-tetrakis(trifluoromethyl)benzene (**1**) failed. Addition of alkyl-lithium or phenyl-lithium reagents to a solution of compound **1** in diethyl ether at temperature above 0 °C resulted in the immediate formation of a brown tar from which no individual compound could be isolated. The reaction conducted at low temperature, preferably at −78 °C, formed deeply coloured solutions stable up to *c.* −40 °C; above this temperature the colour faded and a brown tar was again formed. The solutions failed to react with carbon dioxide and other electrophilic reagents, but quenching with acids or water gave, beside some tar, mixtures of unreacted **1** and chromatographically isolable products **2a–2c** of the general formula $C_{10}H_2F_{10}R_2$ (Scheme 2). Variation of the ratio of organolithium reagents to tetrakis(trifluoromethyl)benzene did not influence the elemental composition of the products.



R	Colour		%	%
n-Bu	deep-red	**2a**	31	21
tert-Bu	purple-violet	**2b**	54	18
Ph	orange	**2c**	34 (2 compd. 10:1)	12
Me	deep-green	**2d**	50 (4 compd.)	20

Scheme 2.

Quenching the reactions with D_2O did not result in the formation of the deuterated derivative of compound **1**, which excludes recovery of the substrate via protonation of the respective lithium derivative.

Analysis of compounds **2** suggests that they are, at least formally, products arising from the substitution of two fluorine atoms in **1** by butyl groups.

Reaction with t-butyl-lithium proceeded most cleanly and gave the highest yield of the dialkyl-substituted product **2b**. In the case of phenyl-lithium, two isomeric compounds **2c** and **2c′** were formed in a 10:1 ratio. Reaction with methyl-lithium gave at least four, hardly separable compounds **2d**; for this reason, we have not attempted their isolation or identification.

An X-ray analysis of the crystalline diphenyl derivative **2c** gave unequivocal proof for its structure as a mixture of enantiomeric 7-fluoro-4,7-diphenyl-2,4,5-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (Fig. 1). The atomic co-ordinates are given in Table 1, and selected skeletal bond lengths and bond angles in Tables 2 and 3.

Compound **2c** is obviously a non-aromatic molecule. It contains a 2,5-cyclohexadiene ring with one exocyclic double bond terminated with a single fluorine and the phenyl group. The second phenyl group is bound to the ring carbon atom 4, together with one trifluoromethyl group. The other two trifluoromethyl groups are in positions 2 and 5, and the protons occupy positions 3 and 6 (not shown in Fig. 1).

The ^1H and ^{19}F NMR spectra of the diphenyl derivative **2c** and other compounds of the series, i.e. **2a**, **2b**, and **2c′**, show great similarity, thus confirming the cyclohexadiene–ylidene structure of all these compounds (Fig. 2).

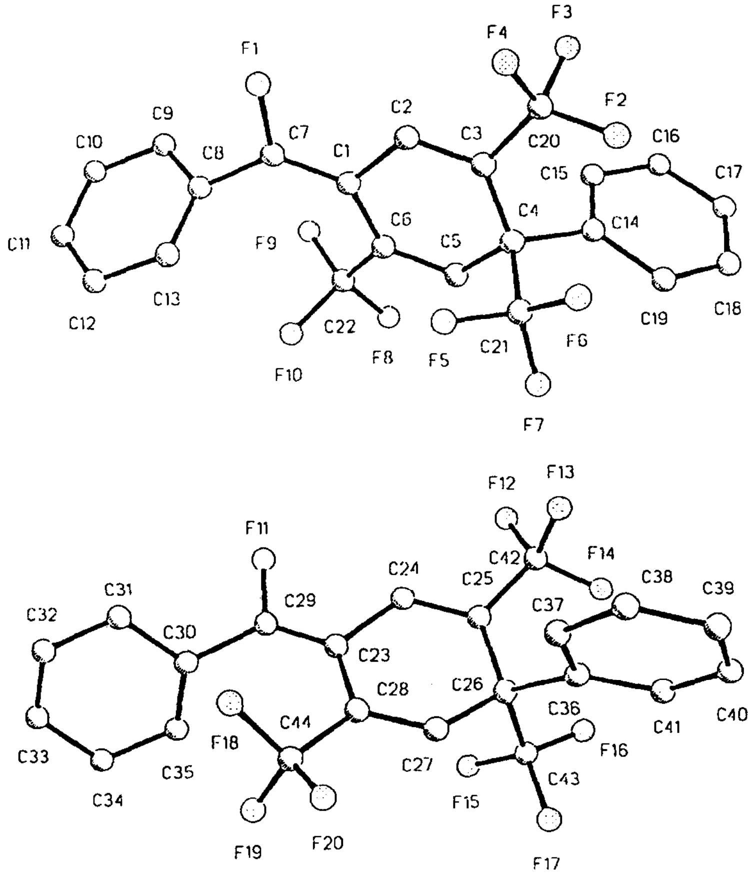
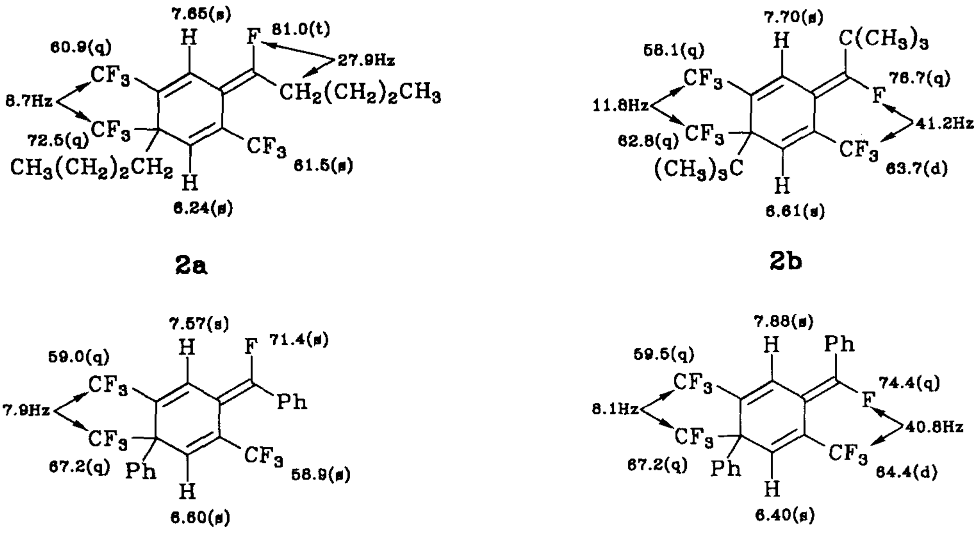


Fig. 1. X-Ray molecular structure of *R*/*S*-7-fluoro-4,7-diphenyl-2,4-5-tris(trifluoromethyl)-2,5-cyclohexadiene-1-ylidene (**2c**) with crystallographic numbering. Hydrogen atoms and double bonds are not shown.

The proton NMR spectra exhibit, beside absorptions corresponding to the phenyl or alkyl substituents, two signals in the range *c*. 7.5 and 6.5 ppm, i.e. *c*. 0.8 and 1.8 ppm respectively upfield from the signal corresponding to the aromatic protons of the starting tetrakis(trifluoromethyl)benzene (8.34 ppm).

The fluorine spectra show the presence of three non-equivalent CF_3 groups and a signal of a single vinylic fluorine. Strong coupling between the vinylic fluorine and the neighbouring trifluoromethyl group gives evidence for their mutual *cis* orientation in the minor isomer of diphenyl compound **2c′** and in the t-butyl derivative **2b**. In the n-butyl derivative **2a**, similarly to the major diphenyl-substituted compound **2c**, the vinylic fluorine and the CF_3 group are in a *trans* configuration; splitting of the vinylic fluorine signal into a triplet is due to coupling with the CH_2 group. Generally, the preferential



2a **2b**

2c (major) **2c'** (minor)

Fig. 2. ^1H and ^{19}F NMR data (measured in $CDCl_3$) for compounds **2a**, **2b**, **2c** and **2c'**. Chemical shifts are in ppm from internal TMS for the proton nuclei (positive downfield) and from internal CCl_3F for the fluorine nuclei (positive upfield).

position of the vinylic fluorine in relation to the ring CF_3 group is *trans*; however bulky substituents such as the t-butyl group reverse this preference.

The ^{13}C NMR spectra of compounds **2** (see Experimental section) also confirm the presence of three non-equivalent trifluoromethyl groups and a vinylic carbon bearing a single fluorine atom ($^1J(C–F) = 272–284$ Hz). The presence of two CH groups is shown by signals with coupling constants $^1J(C–H) = 160–167$ Hz in non-proton decoupled spectra.

The logical mechanistic interpretation for the formation of cyclohexadiene–ylidene derivatives **2** in reactions of 1,2,4,5-tetrakis(trifluoromethyl)benzene (**1**) with organolithium reagents seems to be as shown in Scheme 3.

The first step apparently involves nucleophilic addition of an alkyl or aryl group of the organolithium reagent to one of the benzene ring carbon atoms of **1** and elimination of fluoride ion from the opposite trifluoromethyl group. The intermediate terminal difluoroalkene (**i**) should be expected to be very susceptible to nucleophilic attack and it immediately reacts with the second molecule of the organolithium reagent via an addition–elimination mechanism (intermediate **ii**), which results in substitution of the terminal vinylic fluorine by an alkyl or aryl group to give the dearomatised product **2**. A similar mechanism has been proposed for the reaction of hexakis(trifluoromethyl)benzene with ammonia leading to substitution of trifluoromethyl groups by cyanide groups [3]. In that mechanism, the structure of the first intermediate was identical to the structure of products **2** formed

TABLE 1.

Atomic coordinates for structure **2c**

Atom	*x/a*	*y/b*	*z/c*
C-1	1211(4)	8516(12)	4692(4)
C-2	1157(4)	9939(12)	5028(3)
C-3	1260(4)	9778(12)	5570(4)
C-4	1444(5)	8052(12)	5878(3)
C-5	1647(5)	6743(13)	5544(4)
C-6	1538(4)	6874(12)	5003(4)
C-7	997(4)	8786(13)	4135(3)
C-8	859(5)	7662(12)	3649(3)
C-9	1185(6)	8010(14)	3294(4)
C-10	1018(7)	7007(19)	2806(4)
C-11	532(7)	5660(18)	2680(4)
C-12	199(6)	5343(15)	3030(5)
C-13	372(5)	6342(14)	3514(4)
C-14	2093(5)	8250(12)	6445(3)
C-15	2687(4)	9027(14)	6427(4)
C-16	3295(5)	9213(15)	6912(4)
C-17	3297(5)	8674(16)	7416(4)
C-18	2722(2)	7885(16)	7441(4)
C-19	2099(5)	7660(14)	6950(3)
C-20	1201(6)	11447(14)	5852(4)
C-21	815(5)	7303(14)	5955(3)
C-22	1784(5)	5474(14)	4741(4)
C-23	3536(4)	3629(12)	4712(4)
C-24	3899(5)	5134(13)	5042(3)
C-25	4295(5)	5071(12)	5594(4)
C-26	4409(5)	3384(13)	5921(4)
C-27	3898(4)	2027(12)	5589(4)
C-28	3525(5)	2088(12)	5040(4)
C-29	3235(5)	3870(12)	4152(4)
C-30	2906(5)	2628(13)	3684(3)
C-31	2221(5)	2963(15)	3311(4)
C-32	1930(6)	1880(17)	2845(4)
C-33	2315(7)	617(19)	2747(4)
C-34	2999(6)	274(16)	3112(4)
C-35	3281(5)	1331(15)	3574(4)
C-36	4298(4)	3696(12)	6465(3)
C-37	3634(5)	3961(13)	6422(4)
C-38	3460(6)	4287(15)	6870(4)
C-39	3999(6)	4411(14)	7400(4)
C-40	4665(6)	4126(15)	7450(4)
C-41	4819(5)	3816(14)	6992(4)
C-42	4580(5)	6868(15)	5868(4)
C-43	5117(5)	2567(13)	6027(4)
C-44	3014(5)	527(15)	4789(4)
F-1	814(3)	10481(7)	3967(2)
F-2	1217(4)	11279(8)	6359(2)
F-3	1781(5)	12460(10)	5986(4)
F-4	713(5)	12454(12)	5574(3)

(continued)

TABLE 1. (*continued*)

Atom	*x/a*	*y/b*	*z/c*
F-5	283(3)	7119(8)	5452(2)
F-6	585(3)	8230(7)	6267(2)
F-7	941(3)	5648(7)	6173(2)
F-8	2265(3)	4401(8)	5133(2)
F-9	2109(3)	6022(8)	4420(2)
F-10	1287(3)	4328(7)	4433(2)
F-11	3217(3)	5549(7)	3963(2)
F-12	4634(4)	8027(8)	5526(2)
F-13	4134(3)	7565(8)	6073(3)
F-14	5180(3)	6733(8)	6312(2)
F-15	5185(3)	2225(8)	5551(2)
F-16	5669(3)	3609(8)	6321(2)
F-17	5224(3)	1063(8)	6309(2)
F-18	2383(3)	1153(8)	4437(2)
F-19	3245(3)	552(7)	4500(2)
F-20	2917(3)	396(8)	5180(2)

TABLE 2

Selected bond lengths for structure **2c**

Bond	Distance (Å)	Bond	Distance (Å)
C(1)–C(2)	1.42(1)	C(23)–C(29)	1.36(1)
C(1)–C(7)	1.36(1)	C(23)–C(24)	1.45(1)
C(1)–C(6)	1.51(1)	C(23)–C(28)	1.45(1)
F(1)–C(7)	1.36(1)	F(11)–C(29)	1.36(1)
C(3)–C(2)	1.35(1)	C(25)–C(24)	1.35(1)
C(3)–C(4)	1.50(1)	C(25)–C(26)	1.50(1)
C(3)–C(20)	1.49(2)	C(25)–C(42)	1.54(1)
C(4)–C(5)	1.49(1)	C(26)–C(27)	1.49(1)
C(4)–C(21)	1.52(2)	C(26)–C(43)	1.53(1)
C(4)–C(14)	1.57(1)	C(26)–C(36)	1.55(1)
C(5)–C(6)	1.35(1)	C(27)–C(28)	1.34(1)
C(6)–C(22)	1.46(2)	C(28)–C(44)	1.56(1)
C(7)–C(8)	1.46(1)	C(29)–C(30)	1.48(1)

during reactions of compound **1** with organolithiums. Thus, our results support this type of mechanism for the nucleophilic reactions of poly(trifluoromethyl)benzenes.

Our results have shown dramatic differences in chemical properties between those of mono-, bis- and tris(trifluoromethyl)benzenes and those of 1,2,4,5-tetrakis(trifluoromethyl)benzene (**1**), at least for their reactions with organolithium. Results of studies on the reactions of organolithium compounds with other poly(trifluoromethyl)benzenes will be reported in forthcoming publications.

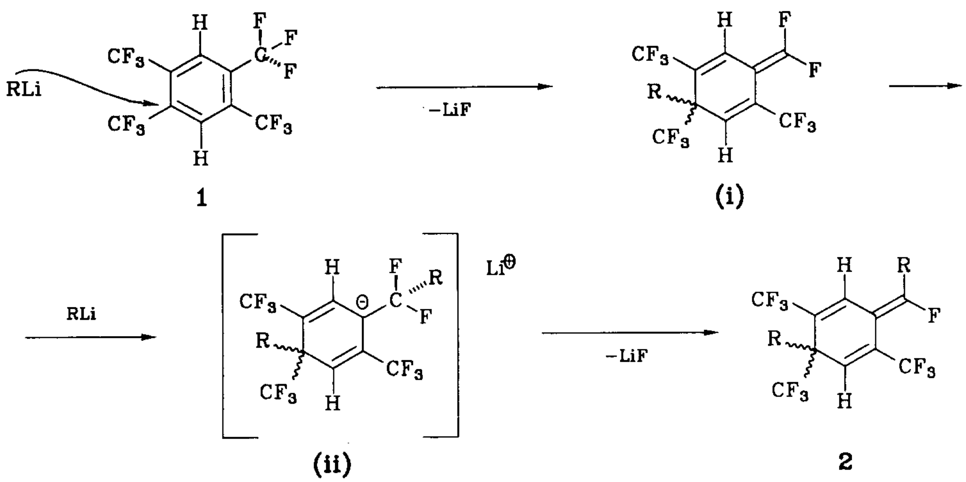
TABLE 3

Selected bond angles for structure **2c**

Bonds	Angle (°)	Bonds	Angle (°C)
C(2)–C(1)–C(7)	118.4(8)	C(29)–C(23)–C(28)	129.5(8)
C(2)–C(1)–C(6)	115.1(7)	C(29)–C(23)–C(24)	116.5(8)
C(7)–C(1)–C(6)	126.5(9)	C(28)–C(23)–C(24)	114.0(7)
C(1)–C(2)–C(3)	124.1(9)	C(25)–C(24)–C(23)	124.3(9)
C(2)–C(3)–C(4)	122.7(9)	C(26)–C(25)–C(24)	122.1(8)
C(2)–C(3)–C(20)	115.6(9)	C(26)–C(25)–C(42)	122.6(7)
C(4)–C(3)–C(20)	121.7(8)	C(24)–C(25)–C(42)	115.2(8)
C(3)–C(4)–C(14)	111.4(7)	C(36)–C(26)–C(25)	110.3(8)
C(3)–C(4)–C(5)	109.7(8)	C(36)–C(26)–C(27)	108.0(8)
C(14)–C(4)–C(5)	106.0(7)	C(25)–C(26)–C(27)	109.8(6)
C(3)–C(4)–C(21)	110.2(8)	C(36)–C(26)–C(43)	112.4(7)
C(14)–C(4)–C(21)	112.4(8)	C(25)–C(26)–C(43)	111.8(9)
C(5)–C(4)–C(21)	106.9(8)	C(27)–C(26)–C(43)	104.3(8)
C(4)–C(5)–C(6)	126.8(8)	C(26)–C(27)–C(28)	125.6(9)
C(1)–C(6)–C(22)	121.1(8)	C(27)–C(28)–C(23)	121.5(8)
C(1)–C(6)–C(5)	119.0(9)	C(27)–C(28)–C(44)	116.1(8)
C(22)–C(6)–C(5)	119.7(8)	C(23)–C(28)–C(44)	121.9(7)
F(1)–C(7)–C(1)	114.8(8)	F(11)–C(29)–C(23)	116.9(8)
F(1)–C(7)–C(8)	109.5(7)	F(11)–C(29)–C(30)	110.9(7)
C(1)–C(7)–C(8)	135.5(9)	C(23)–C(29)–C(30)	132.2(9)
C(7)–C(8)–C(13)	121.5(10)	C(29)–C(30)–C(31)	118.3(9)
C(7)–C(8)–C(9)	119.6(9)	C(29)–C(30)–C(35)	121.1(8)
C(13)–C(8)–C(9)	118.7(9)	C(31)–C(30)–C(35)	120.1(8)
C(8)–C(9)–C(10)	119.8(10)	C(30)–C(31)–C(32)	118.4(10)
C(8)–C(13)–C(12)	122.1(11)	C(30)–C(35)–C(34)	121.6(9)
C(4)–C(14)–C(19)	123.1(9)	C(26)–C(36)–C(41)	125.6(9)
C(4)–C(14)–C(15)	117.3(8)	C(26)–C(36)–C(37)	117.6(7)
C(19)–C(14)–C(15)	119.6(7)	C(41)–C(36)–C(37)	122.1(8)
C(14)–C(15)–C(16)	120.8(9)	C(26)–C(37)–C(38)	123.6(8)
C(14)–C(19)–C(18)	118.5(9)	C(36)–C(41)–C(40)	121.0(1)
F(2)–C(20)–F(3)	97.4(8)	F(12)–C(42)–F(14)	110.2(9)
F(2)–C(20)–C(3)	116.1(9)	F(12)–C(42)–F(13)	105.8(9)
F(3)–C(20)–C(3)	111.6(10)	F(14)–C(42)–C(13)	104.0(8)
F(2)–C(20)–F(4)	109.5(11)	F(12)–C(42)–C(25)	113.7(8)
F(3)–C(20)–F(4)	104.3(9)	F(14)–C(42)–C(25)	113.2(8)
C(3)–C(20)–F(4)	115.8(8)	F(13)–C(42)–C(25)	109.2(9)
F(7)–C(21)–C(4)	111.6(8)	F(15)–C(43)–C(26)	111.2(7)
F(5)–C(21)–C(4)	109.4(8)	F(16)–C(43)–C(26)	114.5(8)
F(6)–C(21)–C(4)	115.8(8)	F(17)–C(43)–C(26)	112.9(9)
F(9)–C(22)–C(6)	115.5(9)	F(18)–C(44)–C(28)	110.0(0)
F(10)–C(22)–C(6)	111.4(7)	F(19)–C(44)–C(28)	111.4(9)
F(8)–C(22)–C(6)	111.4(7)	F(20)–C(44)–C(28)	111.4(7)

Experimental

The ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded at 500, 470 and 125 MHz, respectively, using a Brucker 500 MHz spectrometer and employing



Scheme 3.

$CDCl_3$ solutions. Chemical shifts are listed in ppm from internal TMS for the proton and carbon nuclei (positive downfield) and from internal $CFCl_3$ for the fluorine nuclei (positive upfield). Mass spectra were obtained at 70 eV with an AMD-604 spectrometer.

The X-ray structure analysis of compound **2c** was obtained with a Siemens R3m diffractometer using graphite-monochromated MoK_α radiation. The data were collected with the $\theta/2\Theta$ scan technique (2819 reflections). Crystal data: $C_{22}H_{12}F_{10}$, $M=466.32$, monoclinic, space group $P2(1)/n$; $a=20.920(4)$, $b=7.578(2)$, $c=26.176(5)$ Å; $\beta=113.24(3)°$; $Z=8$, $V=3813.0(3.3)$ Å^3, $D_x=1.625$ g cm^{-3}, $\mu(MoK_\alpha)=1.56$ cm^{-1}. The structure was solved by direct methods using the SHELXTL program. The final reliability factor was $R=0.083$. $R_w=0.075$; weighting scheme: $W=1/\sigma^2(F)+0.000250F^2$. The atomic coordinates, selected bond lengths and bond angles are given in Tables 1, 2 and 3, respectively.

1,2,4,5-Tetrakis(trifluoromethyl)benzene was prepared by treatment of pyromellitic anhydride with sulphur tetrafluoride [9] and purified (>99%) by column chromatography on silica gel (230–240 mesh) using n-hexane as eluant. n-Butyl-lithium, t-butyl-lithium and methyl-lithium were commercial laboratory solutions (FLUKA) in n-hexane, n-pentane and diethyl ether, respectively. Phenyl-lithium was freshly prepared according to the known procedure by refluxing a mixture of benzene, n-butyl-lithium and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in a 4:1:1 molar ratio [10].

General procedure

All reactions were conducted under an atmosphere of dry argon.

n-Butyl-lithium (6 mmol 3.75 ml of a 1.6 M solution in n-hexane) or t-butyl-lithium (6 mmol, 4.7 ml of a 1.4 M solution in n-pentane) was added with a syringe via a rubber septum to a pre-cooled (−78 °C) stirred solution of 1,2,4,5-tetrakis(trifluoromethyl)benzene (**1**) (1.2 g, 3 mmol) in diethyl ether (15 ml) at such a rate as to keep the temperature below −60 °C. In the reaction with phenyl-lithium, a solution of **1** was added to a freshly prepared, pre-cooled solution of the reagent. The reactions were highly exothermic. After addition was complete, stirring was maintained at −70 °C for 1 h and the reaction was then quenched by careful addition of a solution of acetic acid, water or D_2O (7.2 mmol) in tetrahydrofuran (3 ml). After warming up to ambient temperature, the solution was poured into water (100 ml) and extracted with diethyl ether (3×10 ml). The combined extracts were dried ($MgSO_4$), the solvent removed under vacuum and the brownish residue subjected to chromatographic separation on silica gel (230–400 mesh, 1:100 by weight, eluted with n-hexane) to give compounds **2a**, **2b**, **2c** and **2c′** respectively. The corresponding ^{1}H and ^{19}F NMR spectra are given in Fig. 2.

Compound **2a** (R = n-C_4H_9): colourless liquid. Anal.: Found: C, 50.7; H, 5.1; F, 44.0%. $C_{18}H_{20}F_{10}$ requires: C, 50.7; H, 4.7; F, 44.55%. ^{13}C NMR δ: 166.0 (d, =CF, $^{1}J(C-F) = 272$ Hz); 132.2 and 132.1 (dq, CH, $^{1}J(C-H) = 160$ Hz, $^{3}J(C-F) = 7$ Hz); 124.9 (q, CF_3, $^{1}J(C-F) = 286.3$ Hz); 123.5 (q, CF_3, $^{1}J(C-F) = 274$ Hz); 122.3 (q, CF_3, $^{1}J(C-F) = 272.8$ Hz); 126.6 (qd, $\underline{C}-CF_3$, $^{2}J(C-F) = 32$ Hz, $^{2}J(C-H) = 5.5$ Hz); 120.6 (qd, $\underline{C}-CF_3$, $^{2}J(C-F) = 31$ Hz, $^{2}J(C-H) = 6.3$ Hz); 106.3 (d, $\underline{C}=CF$, $^{2}J(C-F) = 20$ Hz); 50.4 (q, $\underline{C}-CF_3$, $^{2}J(C-F) = 27$ Hz) ppm.

Compound **2b** (R = t-C_4H_9): colourless liquid. Anal.: Found: C, 50.5; H, 4.9; F, 45.0%. MS *m/z*: 426 (2%) $M^{+\cdot}$; 369 (2%) $M^{+} - C_4H_9$; 349 (8%); 331 (6%); 313 (14%); 295 (10%); 137 (7%); 57 (100%) $C_4H_9^{+}$; 41 (22%) $C_3H_5^{+}$. ^{13}C NMR δ: 169.9 (d, =CF, $^{1}J(C-F) = 284$ Hz); 133.2 and 132.5 (dm, CH, $^{1}J(C-H) = 162$ and 167 Hz); 125.8 (q, CF_3, $^{1}J(C-F) = 287.4$ Hz); 123.5 (q, CF_3, $^{1}J(C-F) = 273$ Hz); 123.2 (q, CF_3 $^{1}J(C-F) = 273.8$ Hz); 123.4 (q, $\underline{C}-CF_3$, $^{2}J(C-F) = 31$ Hz); 123.3 (q, $\underline{C}-CF_3$, $^{2}J(C-F) = 31.3$ Hz); 105.7 (d, $\underline{C}=CF$; $^{2}J(C-F) = 24.5$ Hz); 56.3 (q, $\underline{C}-CF_3$, $^{2}J(C-F) = 24.2$ Hz) ppm.

Compound **2c** (R = phenyl): pale yellow crystals, m.p., 74–74.5 °c (uncorrected). Anal.: Found: C, 56.5; H, 2.6; F, 40.7%. $C_{22}H_{12}F_{10}$ requires: C, 55.65; H, 2.6: F, 40.75%. MS *m/z*: 466 (12%) $M^{+\cdot}$; 448 (7%); 407 (30%); 397 (100%) $M^{+} - CF_3$; 337 (25%); 319 (45%). ^{13}C NMR δ: 162.0 (d, =CF, $^{1}J(C-F) = 272.4$ Hz); 133.6 and 132.5 (m, CH); 124.7 (q, CF_3, $^{1}J(C-F) = 286$ Hz); 122.6 (q, CF_3, $^{1}J(C-F) = 274.8$ Hz); 122.2 (q, CF_3, $^{1}J(C-F) = 273.3$ Hz); 124.7 (q, $\underline{C}-CF_3$, $^{2}J(C-F) = 33.6$ Hz); 123.8 (q, $\underline{C}-CF_3$, $^{2}J(C-F) = 31$ Hz); 105.3 (d, $\underline{C}=CF$, $^{2}J(C-F) = 20$ Hz); 54.5 (q, $\underline{C}-CF_3$, $^{2}J(C-F) = 28$ Hz) ppm.

Compound **2c′** (R = phenyl: ^{1}H and ^{19}F NMR spectral identification, only.

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References

1 J. F. Harris, R. D. Harder and G. N. Sansen, *J. Org. Chem.*, *25* (1960) 633.
2 L. M. Yagupolskii, V. G. Lukmanov and L. A. Alekseeva, *Zh. Org. Khim.*, *12* (1976) 470.
3 L. M. Yagupolskii, V. G. Lukmanov, V. N. Boiko and L. A. Alekseeva, *Zh. Org. Khim.*, *13* (1977) 2388.
4 J. D. Roberts and D. Y. Curtin, *J. Am. Chem. Soc.*, *68* (1946) 1658.
5 V. G. Lukmanov, L. A. Alekseeva, A. I. Burmakov and L. M. Yagupolskii, *Zh. Org. Khim.*, *9* (1973) 1019.
6 L. Heuer, P. G. Jones and R. Schmutzler, *J. Fluorine Chem.*, *46* (1990) 243.
7 J. Escudie, C. Couret, H. Ranaivonjatoro, M. Lazraq and J. Satge, *Phosphorus and Sulfur*, *31* (1987) 27.
8 G. E. Carr, R. D. Chambers, T. F. Holmes and D. G. Parker, *J. Organometal. Chem.*, *325* (1987) 13.
9 W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, *82* (1960) 543.
10 L. Brandsma and H. D. Verkruijsse, *Preparative Polar Organometallic Chemistry*, Vol. 1, Springer-Verlag, Berlin, 1987, p. 185.