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1 Perfluorohalogenoorgano Compounds of Main Group 1 Elements

1.1 Preliminary Remarks

The compounds of the Main Group 1 elements are covered to the end of 1973 in "Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente" Part 4, 1975 (cited here as Part 4), for further details see the preface of this Supplement Volume.

1.2 Perfluorohalogenoorgano Compounds of Lithium and Sodium

1.2.1 Preparation and Physical Properties

Difluorodilithiomethane CF_2Li_2

Trifluoromethyllithium CF_3Li

Chlorodifluoromethyllithium $ClCF_2Li$

Trifluorovinyllithium $F_2C{=}CFLi$

Difluorodilithiumethylene $F_2C{=}CLi_2$

Chlorodifluorovinyllithium $F_2C{=}CClLi$ and $ClFC{=}CFLi$

The molecular energies for planar and tetrahedral geometries of a number of molecules with a tetracoordinated carbon atom, among them CF_2Li_2, have been surveyed by ab initio MO calculations. It was shown that in the case of CF_2Li_2, the energy of the form with C_2 symmetry, obtained by rotating the FCF plane in the cis planar form by 20° about the angle bisector, is 0.7 kcal/mol lower than the energy of the planar structure, for details see [1].

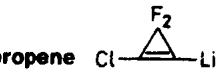
For CF_3Li and $F_2C{=}CFLi$ no new preparations are reported (see Part 4, p. 2), for chemical reactions see Chapter 1.2.2, p. 9.

$ClCF_2Li$ is formed in the reaction of $ClCF_2C(O)OCH_3$ with LiCl in the solvent hexamethylphosphoric triamide and is stabilized by the interaction with the solvent forming a complex [2, 3].

$F_2C{=}CFLi$ is obtained in almost quantitative yield reacting $F_2C{=}CFCl$ and $n\text{-}C_4H_9Li$ in a mixture of tetrahydrofuran, ether and pentane (5:3:3) at −135°C [4]. It also forms in more than 90% yield on adding CH_3Li to a solution of $F_2C{=}CFBr$ in tetrahydrofuran, ether and pentane at −110°C [5].

When $n\text{-}C_4H_9Li$ in ether is added to a solution of $F_2C{=}CCl_2$ in tetrahydrofuran (−120°C, 10 min) and the temperature is then raised to −90°C (5 min), $F_2C{=}CClLi$ is formed in more than 85% yield [6]. In ether as the only solvent the yield lowers to 40% [7], for the dependance of the yield from the ratio of both solvents see [6]. In an ether solution $F_2C{=}CCl_2$ reacts with $n\text{-}C_4H_9Li$ at −70°C (0.5 h) to form $F_2C{=}CClLi$ [8]. $FClC{=}CFLi$ is prepared by the reaction of $ClFC{=}CFCl$ with $n\text{-}C_4H_9Li$ at −115°C in ether/tetrahydrofuran [7].

The barriers of rotation around carbon-carbon double bonds and the relative stability of planar and perpendicular olefins, among them $F_2C{=}CLi_2$, were analysed within the framework of the ab initio unrestricted Hartree-Fock theory in terms of electrostatic, exchange repulsion, polarization, charge transfer, and their coupling interactions [54].

1-Lithium-2-chlorodifluorocyclopropene 

1-Lithiumperfluoro(2,2-dimethylpropane) $(CF_3)_3CCF_2Li$

1-Lithiumperfluoro(3-oxa-4-methylpentane) $(CF_3)_2CFOCF_2CF_2Li$

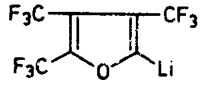
1,6-Dilithiumdodecafluorohexane $Li(CF_2)_6Li$

CNDO/2 calculations with a partial-geometry optimation were carried out on 1-lithium-2-chlorodifluorocyclopropene [9].

The metalation of $(CF_3)_3CCF_2H$ with RLi [R = CH_3, n-C_4H_9, $(CH_3)_3C$] gives $(CF_3)_3CCF_2Li$. The reaction is carried out with CH_3Li in ether and with n-C_4H_9Li or $(CH_3)_3CLi$ in alkane solvents [10].

n-C_4H_9Li in ether reacts with $(CF_3)_2CFOCF_2CF_2I$ at −78°C (1 h) to give $(CF_3)_2CFOCF_2CF_2Li$ [11]; replacing n-C_4H_9Li by C_6F_5Li increases the yield [12].

$Li(CF_2)_6Li$ forms on reacting $Br(CF_2)_6Br$ or $(CH_3)_2SiH(CF_2)_6SiH(CH_3)_2$ in tetrahydrofuran with C_2H_5Li or $(CH_3)_3CLi$ at −190 to −78°C (15 min) or −95°C (12 min), respectively [13].

5-Lithium-2,3,4-tris(trifluoromethyl)furan 

On adding an ether solution of C_4H_9Li at −35°C (1 h, N_2 atmosphere) to a stirred ether solution of 2,3,4-tris(trifluoromethyl)furan the Li-substituted furan forms with further stirring (1 h) [14].

Pentafluorophenyllithium C_6F_5Li

C_6F_5Li is prepared by adding a hexane solution of n-C_4H_9Li to an ether solution of C_6F_5Br or C_6F_5H at −78°C (1 h) [15].

The ion-pair equilibrium between 9-t-butylfluorene (R) and C_6F_5H in cyclohexylamine according

$$R^-Li^+ + C_6F_5H \rightleftharpoons RH + C_6F_5^-Li^+$$

is covered in [16]

Perfluoro(4-methylphenyl)lithium 4-CF_3-C_6F_4Li

1,2-, 1,3- and 1,4-Dilithiumtetrafluorobenzene 1,2-Li_2-C_6F_4, 1,3-Li_2-C_6F_4, 1,4-Li_2-C_6F_4

1,3,5-Trilithiumtrifluorobenzene 1,3,5-Li_3-C_6F_3

At −30°C (0.5 h) C_4H_9Li reacts with 4-Br-$C_6F_4CF_3$ to form 4-CF_3-C_6F_5Li [17]. On adding an ether solution of 1,2-Br_2-C_6F_4 to a stirred hexane solution of C_4H_9Li over 50 min, followed by stirring for further 35 min, 1,4-Li_2-C_6F_4 is formed. 1,2-Li_2-C_6F_4 is obtained on adding n-C_4H_9Li in hexane over 23 min to 1,2-Br_2-C_6F_4 in ether, with further stirring (70 min) [18]. Similar reactions between n-C_4H_9Li and 1,3-H_2-C_6F_4, 1,3-Br_2-C_6F_4 or 1,4-Br_2-C_6F_4 in ether at −70°C (about 2 h, stirring) form the corresponding title compounds [19].

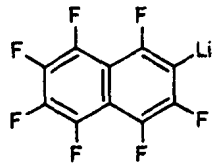
1,3,5-Trifluorobenzene was metalated with n-C_4H_9Li in ether forming 1,3,5-Li_3-C_6F_3 [20].

4-Lithiumtetrafluorophenylperfluoropolyether 4-Li-$C_6F_4CF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

4-Lithiumtetrafluorobenzoylperfluoropolyethers 4-Li-$C_6F_4C(O)R_f$,
R_f = $CF(CF_3)OC_3F_7$, $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$, $CF(CF_3)[OCF_2CF(CF_3)]_4OC_3F_7$, $CF_2(OC_2F_4)_2OC_2F_5$, $CF_2(OCF_2)_3OCF_3$

The first compound forms by the reaction of a tetrahydrofuran/ether solution of 4-Br-$C_6F_4CF_2CF(CF_3)OCF_2CF(CF_3)OC_3F_7$ with a hexane solution of C_4H_9Li. The other compounds are obtained by similar reactions with 4-Br-benzoyl compounds as starting materials [21].

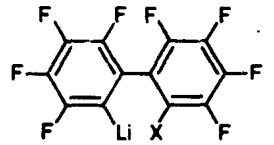
Heptafluoro-2-naphthyllithium



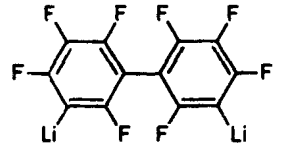
2-Lithiumnonafluorobiphenyl X = F

2-Lithium-2′-bromooctafluorobiphenyl X = Br

2,2′-Dilithiumoctafluorobiphenyl X = Li

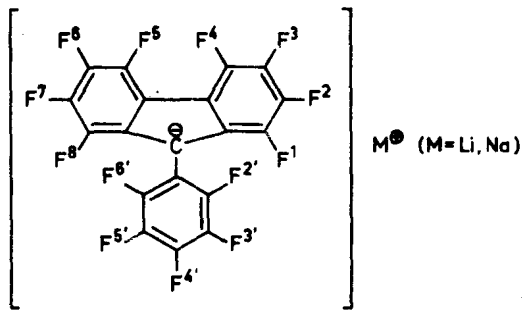


3,3′-Dilithiumoctafluorobiphenyl 3,3′-Li_2-C_6F_4-C_6F_4



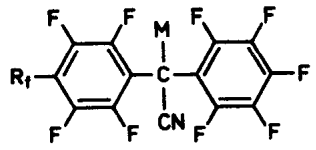
In an ether-hexane mixture, 2-H-heptafluoronaphthalene was reacted with C_4H_9Li at −75°C (2 h) under N_2 to yield heptafluoro-2-naphthyllithium [22, 23]. Lithiation of 2,2′-dibromooctafluorobiphenyl took place in ether at −78°C by adding a hexane solution of n-C_4H_9Li with stirring over a period of 40 min. After additional stirring for 1.5 h 2-lithium-2′-bromooctafluorobiphenyl is obtained. Similarly 2-lithiumnonafluorobiphenyl was prepared from 2-bromononafluorobiphenyl and n-C_4H_9Li, and 2,2′-dilithiumoctafluorobiphenyl by the reaction of 2,2′-dibromooctafluorobiphenyl and n-C_4H_9Li [24]. In tetrahydrofuran 3,3′-H_2-C_6F_4-C_6F_4 and n-C_4H_9Li, dissolved in hexane, reacted at −76°C (2.0 h) to give 3,3′-Li_2-C_6F_4-C_6F_4 [19].

Perfluoro(9-phenylfluorenyl)lithium and -sodium



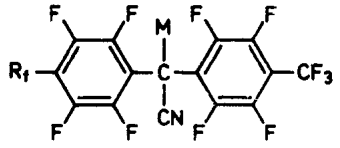
$M^{\oplus}$ (M = Li, Na)

Perfluoro(4-alkylphenyl)pentafluorophenylcyanomethyllithium and -sodium



M = Li, Na, R_f = CF_3, C_2F_5, $CF(CF_3)_2$, $C(CF_3)_3$

Perfluoro(4-alkylphenyl)perfluoro(4-methylphenyl)cyanomethyllithium and -sodium



M = Li, Na, R_f = CF_3, C_2F_5, $CF(CF_3)_2$, $C(CF_3)_3$

9-Hydroperfluoro(9-phenylfluorene) reacts with LiH or NaH in 1,2-dimethylether at 20 to 25°C (1 h) to form the lithium and sodium salts. In the following is given the ^{19}F NMR spectrum of the lithium salt, which is almost identical with that of the sodium compound (chemical shifts δ in ppm have a positive sign downfield from the internal standard C_6F_6, dimethylether as solvent): $\delta(F^3,F^6) = -17.3$, $\delta(F^2,F^7) = -6.6$, $\delta(F^{3'},F^{5'}) = -3.8$, $\delta(F^{4'}) = 0.0$, $\delta(F^1,F^8) = 2.9$, $\delta(F^4,F^5) = 19.8$, $\delta(F^{2'},F^{6'}) = 23.2$, $J(F^1\text{-}F^2) = 20.5$ Hz, $J(F^1\text{-}F^3) \approx 9$ Hz, $J(F^1\text{-}F^4) \approx 9$ Hz, $J(F^2\text{-}F^3) = 20.5$ Hz, $J(F^3\text{-}F^4) = 19$ Hz, $J(F^1\text{-}F^{2'}) \approx 4$ Hz, $J(F^{3'}\text{-}F^{4'}) = 21.5$ Hz [25]. The difference of the chemical shifts of the perfluoro(9-phenylfluorenyl)ion and of 9-hydroperfluoro-(9-phenylfluorene) is given and discussed in [26].

The metal compounds of the perfluoro(diaryl)cyanomethanes were prepared [27] in dimethylformamide according to

$4\text{-}R_f\text{-}C_6F_4\text{-}CH(CN)\text{-}C_6F_5 + MH \rightarrow 4\text{-}R_f\text{-}C_6F_4\text{-}CM(CN)\text{-}C_6F_5$

and

$4\text{-}R_f\text{-}C_6F_4\text{-}CH(CN)\text{-}C_6F_4\text{-}CF_3\text{-}4' + MH \rightarrow 4\text{-}R_f\text{-}C_6F_4\text{-}CM(CN)\text{-}C_6F_4\text{-}CF_3\text{-}4'$

R_f = CF_3, M = Li, Na; R_f = C_2F_5, M = Li, Na; R_f = $(CF_3)_2CF$, M = Li, Na; R_f = $(CF_3)_3C$, M = Li, Na

The ^{19}F NMR data of the compounds are compiled in **Table 1**, p. 5, and **Table 2**, p. 5.

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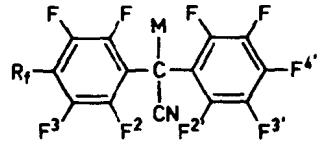
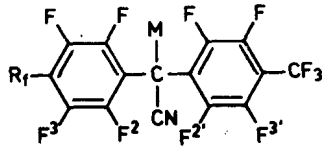
Table 1
^{19}F NMR Spectra of the Lithium and Sodium Compounds of the Following Perfluoro(diaryl)cyanomethanes [27]:



Chemical shift δ in ppm (positive sign means lowfield from the internal standard C_6F_6), spin-spin coupling constant J in Hz, 10 mol% solution in 1,2-dimethoxyethane, [a] ±0.7 ppm, [b] ±0.2 ppm, [c] ±0.5 ppm.

M	R_f	δ(F^2)	δ($F^{2'}$)	δ(F^3)	δ($F^{3'}$)	δ($F^{4'}$)	δ(CF_3)	δ(CF_n)	Absolute J(F-F) coupling constants in Hz
Na	CF_3	15.0[c]	21.5	15.0	−4.3[b]	−4.3[b]	110.2	–	–
Li	CF_3	15.5[c]	21.2	15.5	−3.6[b]	−3.6[b]	110.3	–	–
Na	CF_3CF_2	15.2	21.6	16.1	−3.8[a]	−3.8[a]	77.2	55.4	$J(CF_2\text{-}F^3)$ = 29
Li	CF_3CF_2	15.6	21.4	16.6	−3.5[a]	−3.5[a]	77.1	55.1	$J(CF_2\text{-}F^3)$ = 29, $J(CF_3\text{-}CF_2)$ = 3.3, $J(CF_3\text{-}F^3)$ = 7
Na	$(CF_3)_2CF$	15.8	21.6	20.0	−4.0[a]	−4.0[a]	87.9	−11.4	–
Na	$(CF_3)_3C$	16.2	21.6	27.1	−3.6[a]	−3.6	101.5	–	–
Li	$(CF_3)_3C$	16.9	21.8	27.7	−3.3[a]	−3.3	102.0	–	$J(CF_3\text{-}F^3)$ = 25.7, $J(F^2\text{-}F^3)$ = 14.5

Table 2
^{19}F NMR Spectra of the Lithium and Sodium Compounds of the Following Perfluoro(diaryl)cyanomethanes [27]:



For definitions see Table 1; [a] ±0.6 ppm, [b] 0.6 ppm, [c]: because of poor resolution of the signals the chemical shift value could not be determined exactly.

M	R_f	δ(F^2)	δ($F^{2'}$)	δ(F^3)	δ($F^{3'}$)	δ(4′-CF_3)	δ(CF_3)	δ(CF_n)	Absolute J(F-F) coupling constants in Hz
Na	CF_3	19.5	19.5	16.1	16.1	108.8	108.8	–	$J(CF_3\text{-}F^3)$ = 21.2
Li	CF_3	19.9	19.9	16.5	16.5	108.6	108.6	–	$J(CF_3\text{-}F^3)$ = 21.5
Na	CF_3CF_2	19.9[a]	19.9	17.5	16.8	108.9	77.3	54.7	–
Li	CF_3CF_2	20.0[a]	20.0	18.0	16.7	108.2	77.2	54.7	$J(CF_3\text{-}F^3)$ = 29.5, $J(4'\text{-}CF_3\text{-}F^{3'})$ = 20.5
Na	$(CF_3)_2CF$	20.1[b]	20.1	20.1	16.5	109.0	87.9	−12.5	–
Li	$(CF_3)_2CF$	20.2[b]	20.2	21.1	16.8	109.1	88.0	−12.8	$J(4'\text{-}CF_3\text{-}F^{3'})$ = 21.0, $J(CF\text{-}F^3)$ = 39.5, $J(CF_3\text{-}F^3)$ = 12.5, $J(CF_3\text{-}CF)$ = 6

Table 2 (continued)

M	R_f	$\delta(F^2)$	$\delta(F^{2'})$	$\delta(F^3)$	$\delta(F^{3'})$	$\delta(4'\text{-}CF_3)$	$\delta(CF_3)$	$\delta(CF_n)$	Absolute J(F-F) coupling constants in Hz
Na	$(CF_3)_3C$	20.4[c)]	20.4	28.2	16.3	108.9	101.8	–	–
Li	$(CF_3)_3C$	20.9	20.6	28.9	16.8	109.0	102.4	–	$J(4'\text{-}CF_3\text{-}F^{3'}) = 21.5$, $J(CF_3\text{-}F^3) = 25.9$, $J(F^2\text{-}F^3) = 11.0$

Tris(pentafluorophenyl)methylsodium $(C_6F_5)_3CNa$ and **-lithium** $(C_6F_5)_3CLi$

Bis(pentafluorophenyl)-4-chlorotetrafluorophenylmethylsodium
M = Na, X = Cl

Bis(pentafluorophenyl)-4-bromotetrafluorophenylmethylsodium
M = Na, X = Br

Bis(pentafluorophenyl)-4-trifluoromethyltetrafluorophenylmethyllithium and **-sodium** M = Li, Na; X = CF_3

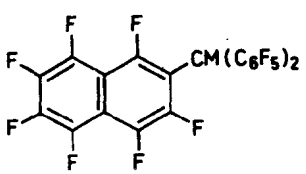
} $(C_6F_5)_2(4\text{-}X\text{-}C_6F_4)CM$

Bis(pentafluorophenyl)-3-chlorotetrafluorophenylmethyllithium and **-sodium** $(C_6F_5)_2(3\text{-}Cl\text{-}C_6F_4)CM$ (M = Li, Na)

Bis(pentafluorophenyl)-3,5-dichlorotrifluorophenylmethylsodium $(C_6F_5)_2(3,5\text{-}Cl_2\text{-}C_6F_3)CNa$

Bis(pentafluorophenyl)pentachlorophenylmethylsodium $(C_6F_5)_2(C_6Cl_5)CNa$

Bis(pentafluorophenyl)heptafluoro-2-naphthylmethyllithium and **-sodium** (M = Li, Na)



To a solution of $(C_6F_5)_2CHR$ in hexamethylphosphoric triamide, NaH was added and the solution stirred at 20 to 25°C (5 to 10 h). The replacement of H by Na takes place according to:

$$(C_6F_5)_2CHR + NaH \rightarrow (C_6F_5)_2CNaR + H_2$$

R = C_6F_5, 4-Cl-C_6F_4, 4-Br-C_6F_4, 4-CF_3-C_6F_4, 3-Cl-C_6F_4, 3,5-Cl_2-C_6F_3, C_6Cl_5, heptafluoro-2-naphthyl ($C_{10}F_7$).

In a similar way, lithium compounds were prepared using $(C_6F_5)_2CHR$ with R = C_6F_5, 4-CF_3-C_6F_4, 3-Cl-C_6F_4, heptafluoro-2-naphthyl [17]. The ^{19}F NMR data of these compounds are given in **Table 3**, p. 7.

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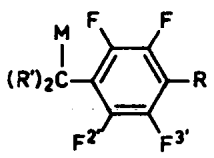
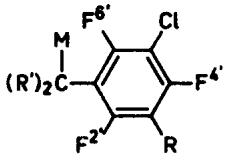
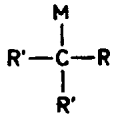
Table 3
^{19}F NMR Spectra of the Compounds A, B, and C [17].



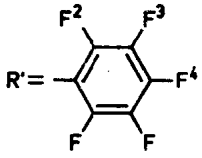
A



B



C



Chemical shift δ in ppm, positive sign lowfield from the internal standard C_6F_6, spin-spin coupling constant J in Hz, concentration of the compounds 10 mol% in hexamethylphosphoric triamide.

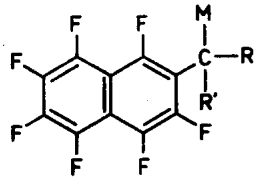
Compound	M	R	δ(R)	δ(F^2)	δ($F^{2'}$)	δ(F^3)	δ($F^{3'}$)	δ(F^4)	δ($F^{4'}$)
A	Na	F	14.6	−17.5	−17.5	6.1	6.1	14.6	δ(R)
A[a]	Li	F	15.0	−17.3	−17.3	6.4	6.4	15.0	δ(R)
A	Na	Cl	–	−17.9	−17.9	6.0	−13.7	12.9	–
A	Na	Br	–	−18.3	−18.3	6.1	−21.0	12.9	–
A	Na	CF_3	−111.2	−19.8	−13.9	5.2	−13.9	8.2	δ(R)
A[b]	Li	CF_3	−111.8	−19.3	−14.0	5.2	−14.0	8.2	δ(R)
B	Na	F	4.8	−17.3	−23.3 −41.6($F^{6'}$)	6.1	δ(R)	14.7	− 6.7
B[c]	Li	F	4.8	−17.3	−23.3 −41.5($F^{6'}$)	6.0	δ(R)	14.7	− 6.8
B[d]	Na	Cl	–	−16.8	−46.6	6.6	–	15.4	−28.5
C	Na	C_6Cl_5	–	−17.5	–	6.4	–	15.4	–
C	Na	$C_{10}F_7$	–	−18.6	–	5.8	–	10.9	–
C	Li	$C_{10}F_7$	–	−19.1	–	5.5	–	10.8	–

[a] $J(F^3\text{-}F^4)$ = 21.8, $J(F^2\text{-}F^4)$ = 7.0, $J(F^2\text{-}F^3)$ = 19.0 Hz. – [b] $J(F^3\text{-}F^4)$ = 22.0, $J(CF_3\text{-}F^{3'})$ = 3.8 Hz. – [c] $J(F^3\text{-}F^4)$ = 22.5, $J(R\text{-}F^{6'})$ = 6.0, $J(F^{2'}\text{-}F^{4'})$ = 10, $J(F^{2'}\text{-}F^{6'})$ = 4.0, $J(F^2\text{-}F^{2'})$ = $J(F^{4'}\text{-}F^{6'})$ = 0, $J(R\text{-}F^{2'})$ = $J(R\text{-}F^{4'})$ = 23.8 Hz. – [d] $J(F^3\text{-}F^4)$ = 22.5, $J(F^{2'}\text{-}F^{4'})$ = 4.5, $J(F^2\text{-}F^4)$ = 7.5, $J(F^2\text{-}F^{2'})$ = 0 Hz.

Heptafluoro-2-naphthyldicyanomethylsodium R = R′ = CN; M = Na

Heptafluoro-2-naphthylpentafluorophenylcyanomethyllithium and **-sodium**
R = C_6F_5, R′ = CN; M = Li, Na

Heptafluoro-2-naphthyl-4-tetrafluoropyridylcyanomethyllithium and **-sodium**
R = 4-C_5F_4N, R′ = CN; M = Li, Na



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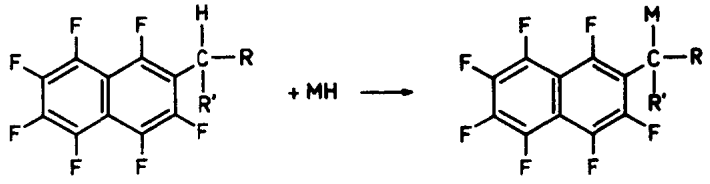
Bis(heptafluoro-2-naphthyl)cyanomethylsodium
R = β-heptafluoronaphthyl, R′ = CN; M = Na

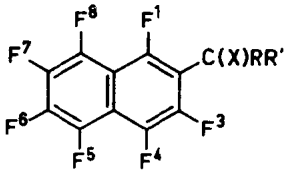
Heptafluoro-2-naphthylbis(pentafluorophenyl)methylsodium and **-lithium**
R = R′ = C_6F_5; M = Li, Na

Heptafluoro-2-naphthylmethanes react in 1,2-dimethoxyethane or hexamethylphosphoric triamide under dry nitrogen with LiH or NaH at 20 to 25°C (4 h) to form the corresponding metalated compounds [28] according to



The ^{19}F NMR spectra are shown in **Table 4**.

Table 4
^{19}F NMR Spectra of the Lithium and Sodium Compounds of the β-Heptafluoronaphthylmethanes [28].



Chemical shift δ in ppm, positive sign lowfield from the internal standard C_6F_6, spin-spin coupling constant J in Hz, HPMA = hexaphosphoric triamide, DME = 1,2-dimethoxyethane, 10 mol% solution in HPMA or DME.

M	R	R′	Solvent	δ(F^1)	δ(F^3)	δ(F^4)	δ(F^5)	δ(F^6)	δ(F^7)	δ(F^8)
Na	CN	CN	HMPA	−34.8	−26.9	− 9.0	−12.4	3.2	−2.5	−12.4
Na	C_6F_5	CN	DME	−36.0	−27.0	− 9.3	−12.8	3.1	−2.3	−12.8
Li[a]	C_6F_5	CN	DME	−36.9	−27.1	− 9.8	−13.6	2.0	−2.9	−13.6
Na	C_6F_5	CN	HMPA	−34.9	−28.0	− 9.0	−12.9	4.6	−2.1	−12.9
Li[b]	C_6F_5	CN	HMPA	−35.1	−28.3	− 9.1	−13.2	4.6	−2.3	−13.2
Na	4-C_6F_4N	CN	DME	−41.8	−28.4	−10.1	−14.3	−2.3	−3.5	−15.3
Li[c]	4-C_6F_4N	CN	DME	−43.0	−29.2	−10.6	−14.9	−2.8	−4.0	−15.8
Na[d]	$C_{10}F_7$	CN	DME	−39.1	−28.3	− 9.7	−14.1	1.1	−2.9	−14.1
Na	$C_{10}F_7$	CN	HMPA	−39.2	−29.6	− 9.6	−14.1	1.6	−3.0	−14.1
Na	C_6F_5	C_6F_5	HMPA	−34.2	−27.5	− 8.3	−12.3	5.7	−1.2	−13.0
Li	C_6F_5	C_6F_5	HMPA	−34.6	−27.9	− 8.3	−12.9	5.5	−1.6	−12.9

[a] $J(F^1\text{-}F^8)$ = 68, $J(F^4\text{-}F^5)$ = 60 Hz. — [b] $J(F^1\text{-}F^8)$ = 65, $J(F^4\text{-}F^5)$ = 56 Hz. — [c] $J(F^1\text{-}F^8)$ = 67, $J(F^4\text{-}F^5)$ = 56 Hz. — [d] $J(F^1\text{-}F^8)$ = 65, $J(F^4\text{-}F^5)$ = 54 Hz.

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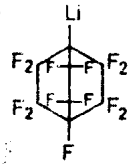
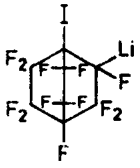
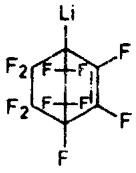
1-Lithiumtridecafluorobicyclo[2.2.2]octane



1-Iodo-2-lithiumdodecafluorobicyclo[2.2.2]octane



1-Lithium-undecafluoro-bicyclo[2.2.2]octa-2-ene



A stirred ether solution of 1-hydrododecafluorobicyclo[2.2.2]octane reacted with CH_3Li at 18°C to give 1-lithiumtridecafluorobicyclo[2.2.2]octane. Refluxing for 70 h leads to a slow loss of LiF to give the transient dodecafluorobicyclo[2.2.2]octa-2-ene. Back addition of LiI affords 1-iodo-2-lithiumdodecafluorobicyclo[2.2.2]octane. 1-Lithiumtridecafluorobicyclo[2.2.2]octane is, at reflux temperature, in equilibrium with 1-lithiumundecafluorobicyclo[2.2.2]octa-2-ene and 1-iodotridecafluorobicyclo[2.2.2]octane [29].

1.2.2 Chemical Reactions

1.2.2.1 Hydrolysis, Carboxylation and Reactions with SO_2

Perfluorohalogenoorgano compounds of the Main Group 1 elements are sensitive to H_2O, acids and bases. They hydrolyse to the corresponding hydrogenated perfluorochlorohydrocarbons and M^+ according to:

$$R_fM + H^+ \rightarrow HR_f + M^+ \ (M = Li, Na)$$

Another typical reaction is CO_2 insertion forming $R_fC(O)OM$; e.g., heptafluoro-2-naphthyllithium reacts with CO_2 at −75°C (0.5 n) to yield the corresponding lithium salt which on treatment with 4 M HCl gives heptafluoro-2-naphthoic acid (melting point 188 to 189°C) [22]. In a similar way 5-lithium-2,3,4-tris(trifluoromethyl)furan gave 2,3,4-tris(trifluoromethyl)-5-furancarboxylic acid in 72.8% yield (melting point 81°C) [14].

For the preparation of octafluoro-9-fluorenone and 2,2′-octafluorodiphenic acid using this method, see [24].

Perfluorohalogenoorganolithium compounds are very reactive intermediates and are used in situ for further reactions. They are often used for the preparation of the title compounds, e.g. [30]:

$$F_2C{=}CFLi + SO_2 \rightarrow F_2C{=}CFSO_2Li \xrightarrow{H^+} F_2C{=}CFSO_2H$$

Therefore, these types of reactions are not recorded here.

1.2.2.2 Thermal Stability. Reactions with Br_2 and I_2

The enthalpy of the decomposition of $LiCF_3$ according to

$$LiCF_3 \rightarrow LiF + CF_2$$

has been calculated by thermodynamic data to be 2 kcal/mol. MINDO/3 and MINDO/2 calculations resulted in 2 and 0 kcal/mol, respectively [31].

$(CF_3)_3CCF_2Li$ decomposes in ether on standing overnight at −78°C. Under the same conditions it is much more stable in alkane solutions, which are the solvents of choice for the investigation of the reaction of the carbene species generated by α elimination of LiF [10].

Significant decomposition of $Li(CF_2)_6Li$ occurs at −78°C [13].

At −78°C $(CF_3)_2CFOCF_2CF_2Li$ formed from $n\text{-}C_4H_9Li$ is at least stable for 20 h. When the temperature is raised to −30°C (2 h) decomposition with the formation of $(CF_3)_2CFOCF{=}CF_2$ is observed. When C_6F_5Li was used as starting material $(CF_3)_2CFOCF_2CF_2Li$ was found to be unstable even at −78°C providing $(CF_3)_2CFOCF{=}CF_2$ [12].

Heptafluoro-2-naphthyllithium eliminates LiF on warming from −78 to 20°C to give hexafluoro-1,2-naphthalene, for condensation with excess furan or heptafluoro-2-naphthyllithium see the original paper [23].

1-Iodo-2-lithiumdodecafluorobicyclo[2.2.2]octane decomposes to give 1-iodoundecafluorobicyclo[2.2.2]oct-2-ene. Refluxing 1-lithiumtridecafluorobicyclo[2.2.2]octane results in the formation of dodecafluorobicyclo[2.2.2]octa-2-ene [29].

Iodation of 1-lithiotridecafluorobicyclo[2.2.2]octane with I_2 leads to the corresponding iodo compound [29]. Heptafluoro-2-naphthyllithium reacts with Br_2 to yield 2-bromoheptafluoronaphthalene (melting point 73 to 74°C) [22].

1.2.2.3 Reactions with Organohalogenosilanes, -phosphines, -phosphineoxides, Benzene and Halogenobenzenes

Reactions of C_6F_5Li with the reagents C_6F_5X (X = H, F, Cl, Br, I), $C_6F_4X'_2$ (X' = H, Cl), $C_6F_3Cl_3$, C_6H_6, $(C_6Y_5)_3P$, $(C_6Y_5)_3PO$, $(C_6Y_5)Si(CH_3)_3$ (Y = H, F) and $(CH_3)_{4-n}SiCl_n$ (n = 1, 2) in ether or in ether/n-hexane solution were investigated by GC/MS techniques. For details and results see original paper [15].

An ether solution of C_6F_5Li condenses with $(CH_3)_2(CHCl_2)SiCl$ at −70°C then warming to 20°C forming $C_6F_5Si(CH_3)_2CHCl_2$ (45% yield, boiling point 122°C/50 Torr). IR bands and ^1H NMR chemical shifts are presented. Five more compounds containing a $C_6F_5Si(CH_3)_2$ group were prepared and used as protecting groups for steroid alcohols forming volatile ethers, detectable at picogram levels in gas chromatography [32]. 1,3,5-Trifluorobenzene is metalated by C_6F_5Li in tetrahydrofuran at −70°C and gives 2-lithium-1,3,5-trifluorobenzene, which reacts with $(CH_3)_3SiCl$ to form $2\text{-}(CH_3)_3Si\text{-}1,3,5\text{-}C_6F_3H_2$ (16.1% yield) and $(CH_3)_3SiC_6F_5$ (52%) [20].

C_6F_5Li with $(C_6H_5)_3B$ in a N_2 atmosphere at −78°C (3 h) and then at 20°C (12 h) forms the complex $Li[B(C_6H_5)_3C_6F_5]$. In a similar reaction $Li[B(4\text{-}CH_3\text{-}C_6H_4)_3C_6F_5]$ is prepared [33].

$Li(CF_2)_6Li$ reacts with $(CH_3)_3SiCl$ at −95°C yielding 72% $(CH_3)_3Si(CF_2)_6Si(CH_3)_3$ [13].

Lithiumtridecafluorobicyclo[2.2.2]octane forms with $(CH_3)_3SiCl$ in ether at 18°C (16 h) 1-(trimethylsilyl)tridecafluorobicyclo[2.2.2]octane (melting point 97°C) [29].

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1.2.2.4 Reactions with Alcohol, Ketones and Aldehydes

The decomposition of $ClCF_2Li$ in hexamethylphosphoric triamide in the presence of CF_3CH_2OH at reflux temperature (12 h) gives 100% CHF_2Cl. The lithium compound reacts with ketones under similar conditions according to:

$$ClCF_2Li + RC(O)R' \rightarrow RR'C(OLi)CF_2Cl \xrightarrow{H^+} RR'C(OH)CF_2Cl$$

R, R', boiling point °C/Torr, yield (%): C_6H_5, CF_3, 68 to 70/8; 63%; n-C_4H_9, CF_3, 52 to 53/18, 39%; C_6H_5, CF_2Cl, –, 18%; additional product 50% $C_6H_5CCl{=}CF_2$ [2; 3]. The reaction mechanisms and further reactions are described in [2].

When C_6H_5CHO is added to $F_2C{=}CFLi$ dissolved in a mixture of tetrahydrofuran, ether and pentane (4:1:1) at −60°C (0.5 h), $C_6H_5CH(OH)CF{=}CF_2$ (96% yield) is formed after treatment with 2 N HCl; ^1H NMR data are presented [5]. In a mixture of tetrahydrofuran, ether and pentane (5:3:3), $F_2C{=}CFLi$ reacts with ketones and aldehydes dissolved in ether at −13°C (for acetophenone at −30°C) according to:

$$F_2C{=}CFLi + \underset{\underset{O}{\|}}{RCR'} \rightarrow \underset{\underset{CF{=}CF_2}{|}}{RC(OLi)R'} \xrightarrow{3\ N\ H_2SO_4} \underset{\underset{CF{=}CF_2}{|}}{RC(OH)R'}$$

R, R', boiling point in °C/Torr, n_D^{20}, yield: C_6H_5, CH_3, 40/0.1, 1.4875, 88%; $-(CH_2)_5-$, 36/0.05, 1.4320, 88%; C_6H_5, H, 51/0.1, 1.4865, 83%; C_5H_{11}, H, 37/0.5, 1.3985, 88%. IR bands [ν(C=C)], ^1H and ^{19}F NMR spectra are presented [4].

Cyclohexanone adds $ClCF{=}CFLi$ (at −110°C, then warmed to −80°C, 10 min) to yield after hydrolysis with 6 N H_2SO_4 85% 1-(2-chloro-1,2-difluoroethenyl)-1-cyclohexanol (boiling point 45°C/0.05 Torr). IR bands and ^{19}F NMR data are provided. Similarly $F_2C{=}CClLi$ reacts with n-C_3H_7CHO to give 40% n-$C_3H_7CH(OH)CCl{=}CF_2$ (boiling point 60 to 62°C/13 Torr, n_D^{20} = 1.4185) IR bands and ^{19}F NMR data are given [7]. $F_2C{=}CClLi$ adds ketones and aldehydes according to:

$$CF_2{=}CClLi + R^1R^2C{=}O \rightarrow R_1R_2C(OLi)C(Cl){=}CF_2 \xrightarrow{H^+} R_1R_2C(OH)CCl{=}CF_2$$

R^1, R^2, boiling point in °C/Torr, n_D^{20} and yields are as following: C_6H_5, H, 63 to 64/0.05, 1.5110, 82%; CH_3, CH_3, 37 to 40/13, 1.4160, 70%; $-(CH_2)_5-$, 44 to 45/0.05, 1.4630, 86%; IR[ν(C=C)], ^1H and ^{19}F NMR values are recorded [6]. With cyclohexanone dissolved in ether, $F_2C{=}CClLi$ forms on warming from −70 to 17°C (1.7 h) 62% 1-(1-chloro-2,2-difluorovinyl)cyclohexanol (boiling point 68 to 72°C/8 Torr) [8].

In ether 4-CF_3-C_6F_4Li reacts with $(C_6F_5)_2CO$ to yield after hydrolysis with concentrated HCl 4-trifluoromethyl-2,3,5,6-tetrafluorophenylbis(pentafluorophenyl)carbinol which sublimes at 170°C/5 Torr. IR and ^{19}F NMR spectra are given [17]. Addition of $(CF_3)_2CFOCF_2CF_2Li$ to $(CF_3)_2CO$ at −78°C (3 h) in hexane gives 94% $(CF_3)_2CFOCF_2CF_2C(CF_3)_2OLi$ (boiling point 155 to 157/0.3 Torr) [11].

1.2.2.5 Reactions with Olefins, Cyclopentadiene and $C_6H_5ICl_2$

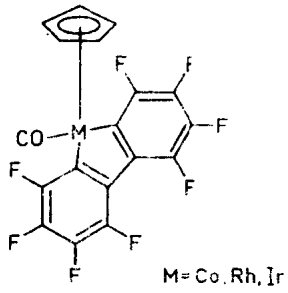
Adding $CF_3CF{=}CF_2$ in the form of a gas to an ether solution of C_6F_5Li in a stream of dry argon between −80 and 50°C, keeping the mixture at −70°C (3 h) and, afterwards acidifying with 10% HCl at 10°C, gives 8% cis-1-perfluoro(phenylpropylene), 40% trans-1-perfluoro-(phenylpropylene), 10% trans-perfluoro[α-(4-biphenyl)propylene] and 5% pentafluorobrombenzene [34]. With excess n-C_4H_9Li dissolved in ether $F_2C{=}CCl_2$ forms at −40°C (0.5 h) 1-hexyne via $F_2C{=}CClLi$ [8]. An etheral solution of C_6F_5Li reacts at −78°C (1 h) with $C_6H_5ICl_2$ to give 23% $C_6F_5(C_6H_5)ICl$ (decomposition point 174°C) [35].

C_6F_5Li reacts with cyclopentadiene in hexane on refluxing (2 h) to yield 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-methanonaphthalene (boiling point 93 to 94°C/18 Torr, melting point 44 to 44.5°C) [36].

1.2.2.6 Reactions with Transition Metal Compounds

When 1,3-$Li_2C_6F_4$ is treated with C_2H_5HgCl in ether at −70°C (2 h) and then at −40°C (3 h), low yields of 1,3-$(C_2H_5Hg)_2$-C_6F_4 are obtained (melting point 75 to 76°C). Treatment of 1,3-Li_2-C_6F_4 with C_2H_5HgCl gave impure 1-C_2H_5Hg-3-Br-C_6F_4 in low yields. In tetrahydrofuran 1,4-Li_2-C_6F_4 reacted with $(CF_3)_2CFHgCl$ at −70°C (0.3 h), then at −40°C (3.5 h) to give 9% 1,4-$[(CF_3)_2CFHg]_2$-C_6F_4 (melting point about 142°C). Condensation of 3,3′-Li_2-C_6F_4-C_6F_4 with C_2H_5HgCl in tetrahydrofuran/hexane at −70°C (2.75 h) gave 39% 3,3′-$(C_2H_5Hg)_2$-C_6F_4-C_6F_4 [19]. The preparation of perfluorobiphenylmercury can be achieved either by the reaction of 2,2′-Li_2-C_6F_4-C_6F_4 and $HgCl_2$ in ether or heating 2,2′-Li_2-C_6F_4-C_6F_4 with Hg at 300°C (melting point >370°C) [37].

In ether (π-C_5H_5)$Co(CO)I_2$ and 2,2′-Li_2-C_6F_4·C_6F_4 are mixed at −78°C. The solution is warmed to 20°C (24 h) giving 49% 5-(π-cyclopentadienyl)-5-carbonyl-1,2,3,4,6,7,8,8-octafluorodibenzocobaltole. The Rh and Ir complex are made similarly [38].



M = Co, Rh, Ir

Norbornadieneplatinum dichloride and 2,2′-Li_2-C_6F_4-C_6F_4 form 3.6% 5,5-norbornadiene-1,2,3,4,6,7,8,9-octafluorodibenzoplatinole. Similar 5,5-di(π-cyclopentadienyl)-1,2,3,4,6,7,8,9-octafluorodibenzozirconole in 4% yield is obtained [38].

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